

Asphaltene Precipitation and Deposition from Crude Oil with CO₂ and Hydrocarbons: Experimental Investigation and Numerical Simulation

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Declaration of Originality

I hereby declare that this thesis is my own work. All published and unpublished sources of information have been appropriately referenced.

Christine Maria Seifried

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Abstract

Asphaltenes are the heaviest and most complex components in crude oil. Their precipitation and deposition may cause severe problems during production, transportation and processing of crude oil, hence affecting efficiency and cost of production in both upstream and downstream operations. During crude oil production, asphaltenes can deposit in the pores of reservoir rocks resulting in formation damage. Despite significant research, asphaltene behaviour in different flow regimes remains elusive. This thesis presents an investigation into crude oil asphaltene precipitation and deposition at ambient and reservoir conditions, using different experimental techniques and multi-scale simulations.

Asphaltene precipitation can be triggered by altering the crude oil composition, which has been studied here through filtration experiments; a useful method to determine the amount of asphaltene precipitation induced by any precipitant. The relationship between the mass of precipitated asphaltenes and the mass of a precipitant in a crude oil+hydrocarbon system was compared to a crude oil+CO₂ mixture in high pressure-high temperature experiments under conditions where the assumption of full miscibility is not valid. The precipitation onset point for the heavy crude oil used throughout the study was precisely determined in terms of the Hildebrand solubility parameter, showing for the first time that CO₂ follows the same behaviour as hydrocarbon precipitants. However, the solubility parameter was not suitable for

correlating precipitation at different temperatures.

Subsequently, this work reports on asphaltene deposition in glass capillary flow experiments under laminar conditions where asphaltenes were precipitated with *n*-heptane, an analogue fluid for CO₂. This study elucidates the fundamental behaviour of asphaltene deposition through the unique combination of techniques not previously been illustrated in the literature. The experiments involved co-injecting a toluene diluted crude oil and *n*-heptane through a capillary at constant volumetric flow rate while simultaneously measuring the pressure drop across the capillary. Increasing the total volumetric flow rate led to more deposition, observed through confocal laser-scanning microscopy and mass measurements, with more deposits build up at the capillary inlet. Beyond a critical flow rate, the deposition rate decreased as entrainment effects became more profound. Deposition was limited as the pressure levelled off in all the experiments, and oscillations in pressure suggested dynamic cycles between deposition and entrainment. In addition, a dependence of deposition on the floc size was revealed, showing that smaller particles dominate the deposition process. The experimental results were then compared to stochastic rotation dynamics simulations at the colloid scale, where a constant pressure drop over the capillary length was imposed. Results show a more homogeneous deposition profile with higher Peclet number, which is in agreement with the experimental findings.

Additionally, deposition studies were extended to real sandstone reservoir samples using C7 and CO₂ as precipitants at more realistic reservoir conditions. Pressure drop measurements across the core to quantify permeability damage were combined with X-Ray Microtomography (microCT) to visualise the deposits produced within the porous medium. The permeability measured through core-flooding experiments was compared to lattice-Boltzmann calculations in the segmented microCT images before and after deposition, where an increase in the flow rate showed a decrease in

dimensionless permeability. Fitting the pressure drop data to a computational Deep Bed Filtration model allowed for a distinction between pore surface and pore throat deposition, which was confirmed by the microCT images of the location of asphaltene deposits. The results elucidate important asphaltene-related issues in porous media and provide a suitable framework for developing and improving deposition models.

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Chapter 1

Introduction

1.1 Energy and Climate Change

One of the major milestones in tackling climate change was the 21st Conference of the Parties (COP21), held in Paris in December 2015. The aim of COP21 for the governments involved was to achieve a global agreement to keep the rise in global average temperature below 2 °C, relative to pre-industrial level, by limiting greenhouse-gas emissions, while sustaining the increase in world economy and supplying billions of people with modern energy. The International Panel on Climate Change (IPCC) has warned that, if no committed and immediate action is being taken, climate change will possibly have drastic and irreversible impacts on the environment.

An analysis by the *International Energy Agency* (IEA 2015) has shown that, as the cost and difficulty of lowering greenhouse-gas emissions continues to increase every year, rapidly addressing these climate issues is of higher importance. The energy sector will therefore play a crucial role in efforts to decrease carbon emissions as currently greenhouse-gas emissions from the energy sector account for approximately two-thirds of all anthropogenic greenhouse-gas emissions with CO₂ emissions

continue to increase.

Recent Developments An important issue in the energy sector has been the rapid drop in the oil prices, and to a lesser extend both gas and coal prices, in 2014/2015. After a long time of relatively constant oil prices, the price has dropped from \$100 per barrel in mid-2014 to below \$40 in end-2015 due to significant oversupply, which was also linked to a weak physical demand and storage capacity issues (OPEC 2015). Despite the low oil prices, the demand for renewables continued to increase in 2014 as they are more cost competitive in several countries though still requiring more public support in many other parts of the world. Power generation by renewables has increased, with new capacity of 128 GW in 2014, of which almost 40% is due to wind power and more than 30% coming from solar power. Oil, however, still remained one of the world's dominant fuels in 2014, even though the world primary energy consumption only grew by 0.9%, which is below average (Figure 1.1).

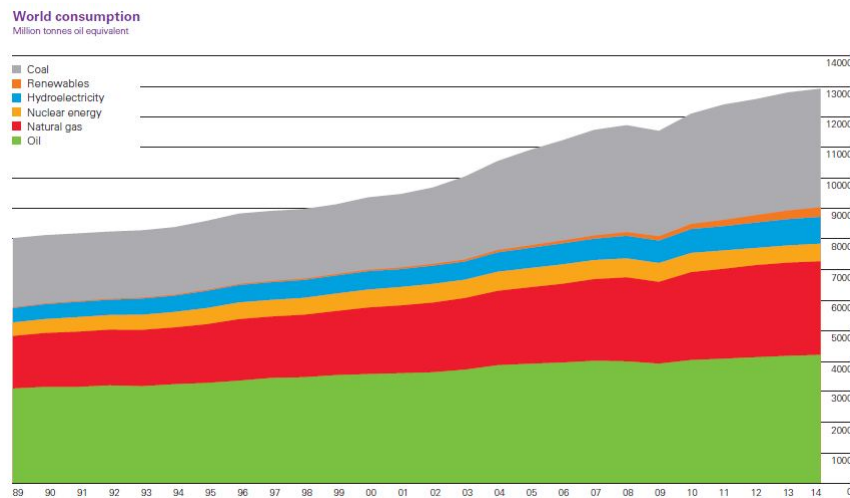


Figure 1.1: World primary energy consumption growth by energy source (BP 2015).

Projecting Future Developments A practice of IEA (2015) is using and describing different scenarios to highlight the impact made by different policy choices

towards climate change and energy supply. One of the three scenarios presented for 2015 is the Intended Nationally Determined Contributions (INDC) scenario which is an assessment of the implications of the choices made by several countries, including among others the European Union, Switzerland, Norway, Mexico and the United States. According to the INDC scenario, the transition away from fossil fuels will be gradual, possibly due to a lack of communication between the participating countries. The fossil fuel proportion of the world's primary energy use is declining from more than 80% today to approximately three-quarter in 2030 (Figure 1.2).

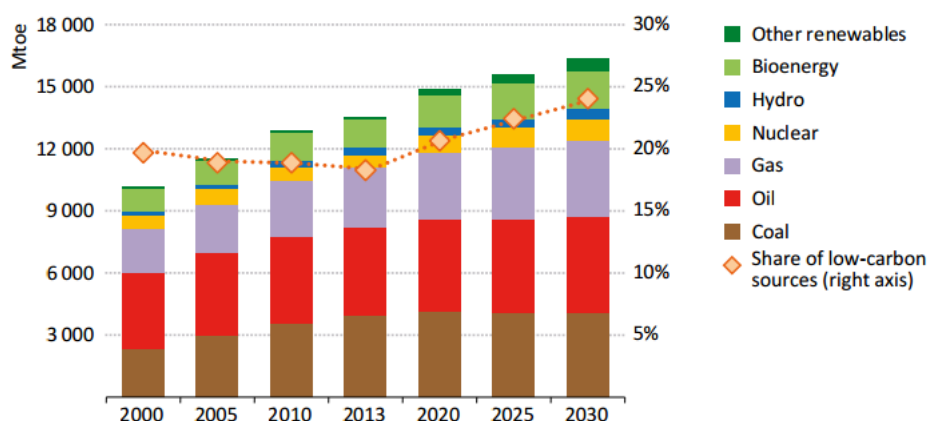


Figure 1.2: Global primary energy demand by type in the INDC Scenario *Note: "other renewables" include wind, solar, geothermal and marine (IEA 2015).*

The coal demand seems to reach a plateau in 2020, however, the trend in OECD regions seems to decline whereas the demand in non-OECD regions continues to increase. The world's oil demand is expected to reach 99 million barrels per day (mb/d) in the year 2030 which is approximately 10% higher than the oil demand today, where most of the growing demand is due to transport sector in the non-OECD regions, particularly in India, China and the Middle East. In the INDC scenario, the world natural gas demand increases by approximately 30% by 2030. Natural gas will aid in emissions control when used as a substitute for other fossil fuels, however,

on the contrary adds to higher emissions when compared to renewables and nuclear. According to the INDC scenario by IEA 2015, natural gas will account for 25% of energy related CO₂ emissions, oil for 34% and finally coal for roughly 41%.

Oil Market Outlook In COP21, 195 countries have come to an ambitious agreement, which means limiting greenhouse-gas emissions, coming mainly from burning of fossil fuels as part of power generation and transport. While many critics conclude that this may mark the end of fossil fuels, this can only be achieved into the second half of this century. According to ExxonMobil (2014), the world primary energy demand will decrease, but both oil and gas will still contribute the major part of energy consumption. An article in DGMK (2014) stated that in the next decades, 70% of the primary energy demand will be covered by fossil fuels, where oil will remain the world's leading fuel. The growth in population will continuously underpin rising energy demand, as the world's population is assumed to increase by 26% to 8.6 billions in 2035, with more than 90% coming from non-OECD regions (IEA 2011). Despite the concerns about climate change and energy security, the demand for oil will continue to increase and the energy sector will continue to rely on oil more than on any other fossil fuel, regardless of the different scenarios made by IEA. Especially developing countries will need to continue to rely on fossil fuels to meet their energy demands.

1.2 Three Phases of Crude Oil Recovery

Due to the increasing demand for crude oil and energy, technologies have advanced to find new unconventional sources and new ways of recovering crude oil from the reservoirs. Crude oil recovery refers to the process by which oil can be extracted from the reservoir beneath the surface. Generally, oil recovery can be classified into three phases:

Primary Recovery

Primary crude oil refers to the first stage of hydrocarbon production, where natural reservoir energy (such as gasdrive and/or waterdrive) can displace the crude oil from the reservoir. Initially, the bottomhole pressure is lower than the reservoir pressure causing a natural pressure drop which then drives the crude oil to the production well. The recovery factor is usually lower than 15-20% of the original oil in place (OOIP) (Marle 1991; Bondor 1992; Ahmed 2006).

Secondary Recovery

During this stage an external fluid such as water or gas is injected into the reservoir. The purpose is to maintain the reservoir pressure and then displace the crude oil. Secondary recovery reaches its limit once the injected fluid is produced from the production wells and allows for additional 10-15% of the oil in the reservoir to be recovered (Bondor 1992).

Tertiary Recovery

The term tertiary recovery is also used as a synonym for “enhanced oil recovery” (EOR). Implementing EOR can increase the recovery via either chemical, thermal, miscible or immiscible flooding. The recovery factor can typically be increased to recover more than 40% of the crude oil available (Bondor 1992; Ayirala and Rao 2004).

1.3 The Link between EOR and Climate Change

Constraining the amount of CO₂ reaching the atmosphere may be achieved by “carbon capture and storage” (CCS). Currently 22 large-scale CCS projects are in operation or under construction with a CO₂ capture capacity of approximately 40 million tonnes (Mt) per year (GlobalCCSInstitute 2014). However, implementing

CCS will eventually contribute to the operating costs of the CO₂ emitting processes, thus increasing fossil fuels energy prices. Therefore, EOR is considered by injecting the captured CO₂ into depleted reservoirs. Since CO₂ is used as a process fluid, it also provides the possibility for long-term storage of CO₂ in the reservoir rock pores after displacing the crude oil. According to Gozalpour et al. (2005), the potential of combining CO₂ storage and EOR is high, where approximately 60% of the CO₂ injected can be retained in the reservoir.

1.4 CO₂ Flooding for EOR

Research about CO₂ injection for EOR has been carried out since 1950 in both laboratory and field studies (Mungan 1984) and subsequently CO₂ for EOR processes has been injected since the early 1970's (Bondor 1992). In general, two variations of CO₂ flooding exist: The miscible process for light and medium gravity oils, and the immiscible process which is best suited for heavy crude oils. The recovery factor can typically be increased by 5-15% when compared to primary and secondary recovery; however, in some fields the recovery can be between 50 and 70% of the OOIP (NETL 2012; Muggeridge et al. 2014).

Usually, CO₂ flooding involves the injection of CO₂ and water, either simultaneously or sequentially. The choice between the different types of applications depends on different factors, for example the direction of oil displacement. Figure 1.3 illustrates the injection of CO₂ and water for EOR purposes. The injected CO₂ moves through the reservoir rock pores and takes residual oil with it. When CO₂ and crude oil are miscible, the interfacial tension between them vanishes and the capillary forces are reduced which enables the CO₂ to displace the oil from the rock pores and pushes it towards the production well. However, the CO₂ does not contact all residual oil in the reservoir. The displacement process will be determined by

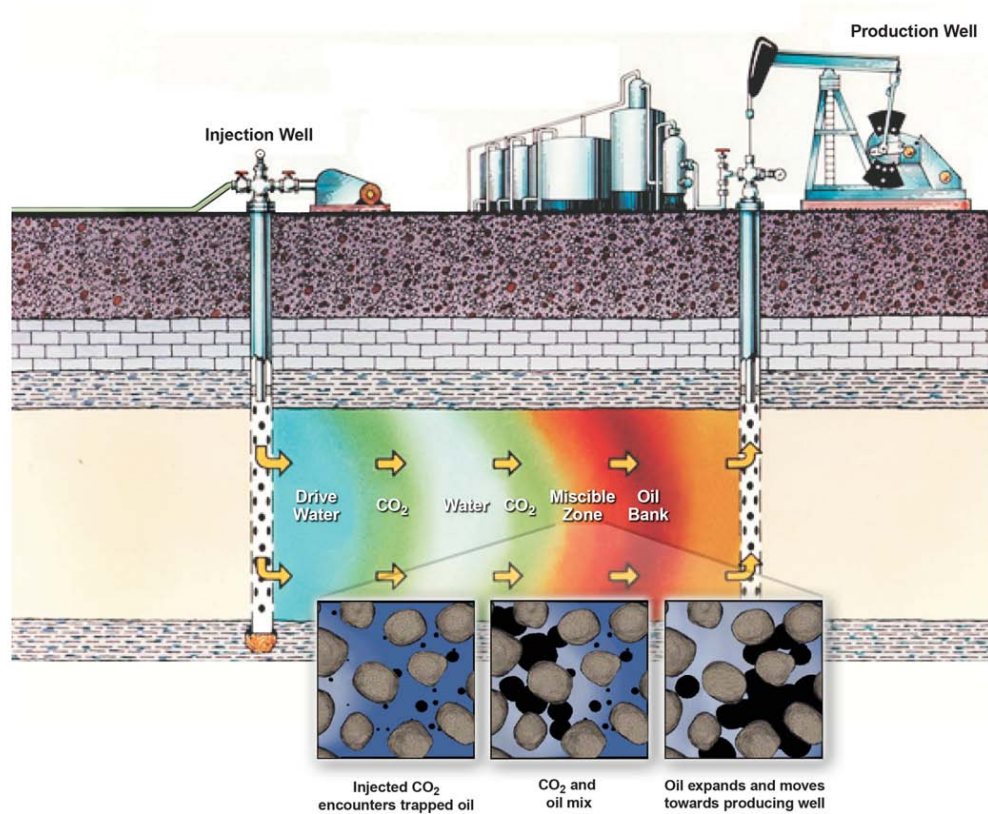


Figure 1.3: CO₂/Water injection for the recovery of residual oil from a subsurface rock formation (NETL 2012).

both rock characteristics (relative permeability and heterogeneity) and fluid property (crude oil viscosity), which affects the mobility (ratio of relative permeability to viscosity) and hence the efficiency of the displacement (Bondor 1992; NETL 2012).

1.4.1 Asphaltene Precipitation during EOR

During CO₂ injection into an oil reservoir, asphaltenes, present in the crude oil, may precipitate, aggregate to flocs and subsequently leading to possible deposition. Precipitated asphaltenes can deposit on the rock surfaces; thus leading to a reduction in the porosity and permeability and eventual blocking of the rock reservoir pores. In addition, asphaltene precipitation and deposition may occur in production wells and

in the pipelines thus giving rise to flow assurance problems. Asphaltene deposition can ultimately lead to serious production problems, hence being one of the costliest challenges the petroleum industry has to deal with (Leontaritis and Mansoori 1987; Zanganeh et al. 2012).

1.5 Project Motivation

This PhD project is aimed at combining carbon storage and enhanced oil recovery (EOR), where the problem of asphaltene deposition due to CO₂ injection in down-hole rock formations on geological time scales will be addressed. Saline aquifers are currently being considered as possible candidate reservoirs for this purpose. However, it is still debatable whether storage in aquifers is economically feasible, thus this project considers depleted oil reservoirs for CO₂ storage, which has the additional effect that CO₂ injected into the reservoir will improve the oil recovery efficiency. A problem arising is that when CO₂ mixes with the crude oil, asphaltene deposition may lead to significant formation damage and reduced oil recovery.

In this project, the fundamental problems associated with these asphaltene phenomena will be investigated by using a combination of experimental and computational techniques. Asphaltene precipitation is yet not fully investigated and understood in the literature and controversy exists under what conditions asphaltene precipitation is initiated. This process is dependent on temperature, pressure and composition changes, however, the main focus in this project lies in the investigation of the change in crude oil composition when exposed to CO₂ at high pressure. Precipitation is a necessary, but not sufficient, requirement for formation damage. Asphaltene must deposit and stick to any surface to become a challenge for flow assurance. Deposition is even more complicated than precipitation as it also depends on flow rate, asphaltene size and size distribution, type of surface and asphaltene-

surface interaction. This work investigates the point at which asphaltenes first start to precipitate from the crude oil and adds to the complex picture of asphaltene deposition, when being precipitated above the onset point.

1.6 Thesis Outline

The thesis is organised as follows:

Chapter 2 reviews the relevant literature associated with asphaltene precipitation and deposition phenomena. A general introduction about asphaltenes is shown in the beginning of the chapter, followed by EOR related issues induced by asphaltene formation damage. Selected literature studies of experimental and computational techniques, relevant to this project, are presented hereafter.

Chapter 3 describes and interprets filtration experiments conducted to understand the asphaltene precipitation induced by hydrocarbons and CO₂. Identifying the conditions under which precipitation occurs is a first step towards a solution to tackle asphaltene deposition problems. The data are reconciled in terms of the Hildebrand solubility parameter, by defining asphaltenes in terms of their solubility with respect to the surrounding solvent. Even though the literature is extensive on the subject of precipitation caused by alkanes, there is a considerable gap on the comparison to CO₂ precipitation studies. In addition, this work addresses the effect of CO₂ solubility in a crude oil on asphaltene stability, which has not been previously accomplished.

Chapter 4 presents the experiments and comparable simulation regarding asphaltene deposition in micro-fluidic capillary flow experiments. A glass capillary is used here as a proxy for a reservoir rock pore. By this simplification a further understanding in the fundamentals leading to deposition is achieved. The conventional approach in capillary flow studies has been relying on transient pressure drop

profiles to assess deposition. The goal of this investigation is to provide a more thorough understanding of asphaltene deposition by incorporating the asphaltene particle size, which relates the extend of deposition to a driving force thus giving further insight into the deposition mechanism.

Chapter 5 extends the work from the previous chapter to deposition studies in porous media through core-flooding experiments, where asphaltenes are precipitated with hydrocarbons and compared to CO₂ induced precipitation at reservoir conditions. The experiments are validated with X-Ray Microtomography images and an empirical model, implemented in a reservoir simulator, which allows for a further assessment of asphaltene damage in a rock core. The advent of pore-scale imaging allows deposits to be seen directly in rock samples, hereby elucidating less addressed issues of asphaltene deposition in porous media.

Chapter 6 concludes the project and discusses further work in several research directions which would build upon the presented work.

Chapter 2

Literature Review

Despite an enormous effort, a fundamental understanding of asphaltene properties has not entirely been achieved yet. From that tremendous, but sometimes also contradictory, amount of work done on asphaltenes a choice on relevant literature related to this project had to be made, which is presented in the following chapter.

This chapter begins by introducing the basic chemistry of asphaltenes in Section 2.1. A definition of a hydrocarbon reservoir and asphaltene related challenges in the petroleum upstream industry will be discussed in Section 2.2. Section 2.3 describes the process of asphaltene precipitation and in particular the concept of the Hildebrand solubility parameter. Section 2.4 examines asphaltene deposition and highlights relevant research related to that phenomenon. Section 2.5 introduces the computational methods used in this thesis for investigating precipitation and deposition and compares between particle and continuum models.

2.1 Asphaltenes

2.1.1 Introduction to Asphaltenes

Asphaltenes are known as the “cholesterol of petroleum” (Boek et al. 2010) due to their ability to precipitate as solids and subsequently deposit with changing pressure, temperature and oil composition. This may affect both surface properties and crude oil rheology. In both up- and downstream operations deposition may cause severe problems. Precipitated asphaltenes can deposit on pipelines, heat exchangers and the bottom of a distillation column; hence they affect efficiency and cost of production. Deposition can lead to fouling or/and damage during oil production or refining. During crude oil production they can deposit in reservoir rock pores, thus leading to possible blocking of flow, particularly in the near well bore region. The asphaltene problem is the most challenging one in petroleum hydrocarbon production, processing and transportation facilities.

Not only the amount of precipitated asphaltenes is important, but also the compatibility between asphaltenes and maltenes that affects rheological properties of crude oils (Bearsley et al. 2004). Therefore knowledge about the formation mechanism of aggregates and crude oil stability is required, as well as other factors that can influence stability and precipitation of the dispersed phase (Laux et al. 1997). To be able to explain the asphaltene behaviour it is necessary to distinguish between precipitation, aggregation and deposition:

Asphaltene precipitation is called the process when asphaltenes become a separate phase from the crude oil. They remain suspended in the liquid phase where the quantity and the size of the asphaltenes are relatively small. The precipitated asphaltenes clump together (**aggregation**) and form larger particles, also called flocs. The asphaltene aggregates are initially suspended in the crude oil (Alian et

al. 2011). Subsequently, the flocs may attach to and accumulate on various surfaces, a process which is called **asphaltene deposition**.

2.1.2 Asphaltene Historical Review and Definition

Asphaltenes were first described by J.B. Boussingault in 1837. He defined “asphaltenes” as alcohol-insoluble, turpentine-soluble solid found in the residue of a distillation (Creek 2005; Buckley 2012).

Crude oil can be divided into the asphaltene and maltene fraction. The maltenes are the continuous oil fraction in which the asphaltenes are dispersed or dissolved (depending on the different views on describing precipitation, more details are provided below). The maltene fraction contains cyclic, saturated and aromatic hydrocarbons with heteroatoms. They are soluble in *n*-alkanes and further separation can be made into resins, aromatic and saturated fraction (Bearsley et al. 2004). The main components in crude oil are therefore saturates, aromatics, resins and asphaltenes, known in the literature as **SARA**. Asphaltenes are the most aromatic of the heaviest components of crude oil (Mullins 2011). The amount of asphaltenes present in crude oil generally varies from one crude oil to another and typically varies from 0% to nearly 20%. They can be defined as a “solubility class”: Asphaltenes are the fraction of the crude oil which is insoluble in light *n*-alkanes (such as *n*-pentane or *n*-heptane) and soluble in aromatic solvents (such as toluene or benzene). Asphaltenes may also be destabilised when CO₂ dissolves into crude oil (Zekri et al. 2007; Rabbani et al. 2012).

2.1.3 Asphaltene Chemistry

2.1.3.1 Asphaltene Structure

Despite a tremendous amount of research during the last half century, a precise molecular asphaltene description still does not exist (Redelius 2006). Asphaltenes exhibit complex structures which comprise one or more polyaromatic units, sulfur and nitrogen linked by alkyl chains (Gray et al. 2011). The architecture can differ in two ways: “Island” and “Archipelago” structure. According to Sabbah et al. (2011), the “Island” structure is the more dominant one, but ongoing debates still question the dominance. The “Island” structure has one single polycyclic aromatic hydrocarbons (PAH) core with cycloalkanes and external branched alkyl substituents, whereas the more recently proposed “Archipelago” structure comprises smaller condensed aromatic groups (Yarranton et al. 2013) (Figure 2.1).

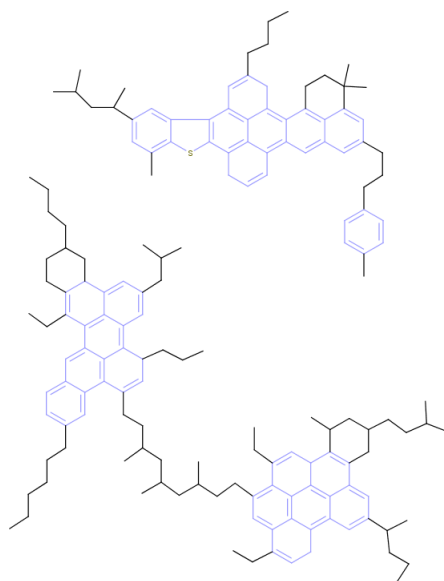


Figure 2.1: Proposed asphaltene structures: “Island” model (top) and “Archipelago” model (bottom).

Molecular asphaltene description is traditionally based on clusters of aromatic

components being surrounded by less aromatic components. From this colloidal point of view, asphaltenes are considered to be a $\pi - \pi$ -bonded stack of continent-like monomers. During the early years of asphaltene research, Pfeiffer and Saal (1940) described the phase separation of highly aromatic components with polar structures promoting dispersion. Recently, Mullins (2010) and Mullins (2011) described the self-formation of aromatic clusters from nanoaggregates by $\pi - \pi$ -stacking of the aromatic rings in crude oil or toluene. This model is also known in the literature as the “Yen-Mullins-Model” and is able to address the molecular description of asphaltene while also supporting the “Island”-model. The concept of self-association was further described by Yarranton et al. (2013) stating that asphaltenes in toluene comprise a mixture of associating and non-associating species. They concluded through, among other techniques, vapour pressure osmometry (VPO) and elemental analysis that approximately 90% of asphaltenes tend to self-associate with the non-associated asphaltenes being smaller and more aromatic than the bulk asphaltenes. According to Gray et al. (2011), however, the description of asphaltene architecture using mainly $\pi - \pi$ -stacking is not sufficient as it is not able to predict or reconcile experimental observations. Therefore, they proposed a new hypothesis on the asphaltene physical structure based on supramolecular assembly combining acid-base interactions, hydrogen bonding and metal coordination complexes in addition to $\pi - \pi$ -stacking.

2.1.3.2 Asphaltene Molecular Weight

There have been many attempts throughout the last years to determine the molecular weight of asphaltenes. Mullins et al. (2012) estimated the molecular weight to about 750 g/mol based on mass spectral methods, with most of the population being between 500 and 1,000 g/mol. However, values in the range of 500 - 12,000 g/mol were found by Waller et al. (1989). Yarranton et al. (2013) approximated the value to 850 g/mol, on the basis of VPO, whereas small angle X-Ray scattering (SAXS)

gave values 10 times larger. According to Yarranton et al. (2013) the discrepancy between SAXS and VPO remained unsolved.

2.2 Asphaltene Issues during Oil Production

Asphaltenes themselves are not problematic, but precipitation and deposition during oil production are a big concern. Light and medium reservoirs are generally good candidates for CO₂ injection as tertiary recovery mechanism, which can, however, lead to precipitation when crude oil is mixed with CO₂. In this section some of the important parameters characterising a reservoir are introduced. A selection of field experiences related to asphaltene issues are reported and literature examples of CO₂ induced precipitation and deposition studies are shown hereafter.

2.2.1 Hydrocarbon Reservoirs

In general, a hydrocarbon reservoir consists of two components: The reservoir rock and the reservoir fluids.

2.2.1.1 Hydrocarbon Reservoir Rocks

The majority of porous media, such as soils and sedimentary rock, contain an interconnected three-dimensional network of channels of non-uniform size and shapes. The so called “pores” usually contain fluids, such as oil or water or a mixture of different fluids. According to Dullien (2012) the macroscopic properties of a porous medium are influenced by the pore structure. The most important pore structure parameters are “porosity” and “permeability”.

Most of the oil reservoirs are made of sandstone, limestone or dolomite formations, where the permeability can vary from fractions of a millidarcy (mD) to 1 Darcy (D) (Bear 1972).

Fundamental Physical Properties of Porous Media Systems

Porosity Porosity (ϕ) is defined as the fraction of bulk volume of the porous sample that is void space and can range between nearly 0 and almost 1 (Dullien 2012; Nimmo 2004). Quantitatively, the porosity is defined as the ratio of the pore volume to the bulk volume (Equation (2.1)) (Ahmed 2006).

$$\phi = \frac{\text{pore volume}}{\text{bulk volume}} \quad (2.1)$$

It can be distinguished between two different types of pores: The first type forms a continuous network within the porous medium and is called the “effective pore space” and the second type is characterized by “isolated” pores or voids. The feature of isolated pores is that they cannot contribute to transport of fluids across the porous medium (Dullien 2012). In reservoir engineering calculations, the value which is used more widely is the effective porosity, since it represents the interconnected pore space containing recoverable hydrocarbon fluids (Ahmed 2006).

Permeability Permeability describes the conductivity of the porous medium, it follows that the rock must be porous in order to be permeable. The unit of permeability is “darcy” and is used to described for unidirectional, steady flow using “Darcy’s law” (Equation (5.7)).

$$Q = -\frac{k}{\mu} \left(\frac{\partial p}{\partial x} - \rho g_x \right) \quad (2.2)$$

where, Q = volume of fluid passing through unit area/unit time; k = permeability; x = flow along x direction; μ = dynamic viscosity; p = applied pressure difference; g_x = gravitational force along the direction of flow (Ahmed 2006).

Furthermore, the permeability can be classified either as “absolute” or “relative” permeability. The term “absolute” refers to the situation, where the rock pores are saturated with a single fluid, whereas the term “relative” is used when more fluids are present in the rock reservoir pores (Lee and Seinfeld 1987).

2.2.1.2 Hydrocarbon Reservoir Fluids

In some instances, oil fields (an oil field can contain several oil reservoirs) are comprised with a segregated gas zone (*gas cap*) overlying the oil part. In undersaturated oil reservoirs, gas caps are not originally present. The part underneath is called the *oil zone*, where liquid hydrocarbons can be found. Deeper in the reservoir, the reservoir rock pores contain only water (*aquifer*) (Marle 1991). The composition of reservoir fluids may vary from region to region. Besides the above named components, other compounds such as oxygen, nitrogen and sulfur can be found (Kokal and Sayegh 1995). Naturally occurring hydrocarbons in reservoirs exhibit multi-phase flow behaviour over a range of pressure and temperature. The differences in phase behaviour and different rock reservoir properties result in a vast variety of hydrocarbon reservoirs with complex behaviours (Ahmed 2006).

2.2.2 Formation Damage and Field Experience

The precipitation of asphaltenes during all three phases of crude oil recovery can lead to a decrease in production efficiency. Leontaritis et al. (1994) stated that generally four forms of formation damage induced by asphaltene deposition can be defined: (i) The physical blockage or permeability reduction, (ii) wettability alteration, (iii) a crude oil viscosity decrease or (iv) the formation of a water-in-oil emulsion. Mechanism (i), however, seems to be the dominant one causing a formation damage. The first step of asphaltene deposition is the adsorption of the asphaltenes on the surface of the rock, followed by hydrodynamic retention and/or

trapping of the particles at the pore throat, eventually leading to a reduction of the effective hydrocarbon mobility (Nghiem et al. 1998; Al-Maamari and Buckley 2003). Zekri et al. (2007) studied the effect of different flow rates in dynamic flow experiments on the change of formation due to asphaltene deposition and stated that a decrease in the flow rate may reduce the formation damage for crude oils with a relatively high content of asphaltenes. According to Kokal and Sayegh (1995), several factors affect the adsorption of asphaltenes on the mineral surface: *(i)* The morphology and chemistry of the mineral surface, *(ii)* the amount of asphaltenes and resins present in the crude oil, *(iii)* the composition and pH of the brines in the reservoir rock and *(iv)* pressure and temperature in the reservoir rock.

Leontaritis and Mansoori (1988) reviewed several experiences of the oil industry dealing with asphaltene issues during production:

Mata-Acema and Boscan field, Venezuela The production field in Mata-Acema is made out of sandstone where the producing fluid contains mainly C7+ fractions with an asphaltene content of 0.4 to 9.8%. The asphaltene issues reported from this field were severe, whereas no asphaltene problems were reported from the Boscan field. The Boscan field is a sandstone and produces mainly heavy oils with an asphaltene content of 17.2%. Alian et al. (2011) and Jafari Behbahani et al. (2012) attributed the differences to the lower solubility of asphaltenes in lighter crude oils in the Mata-Acema field.

Hassi Messaoud field, Algeria The asphaltene content from the stock tank oil produced from the Hassi Messaoud field (sandstone) was measured to be 0.062%. Despite the very low asphaltene content, deposition problems were reported from the start of the production onwards. Wells lost up to 25% of the wellhead pressure in only two weeks, causing significant loss in production.

Ventura Avenue field, California In the Ventura Avenue field asphaltene deposition occurred during primary, secondary and EOR stages. Solvent treatment and circulation of oil were used to avoid or reduce deposition, however, this did not lead to a great improvement of recovery.

2.2.2.1 Asphaltene Deposition during CO₂ Flooding

The following paragraph compares the results of different researchers about asphaltene precipitation induced by CO₂. Negahban et al. (2003) investigated the stability of crude oil after the addition of hydrocarbons and CO₂. The crude oil was believed to be stable with respect to asphaltene precipitation at reservoir conditions. However, the addition of hydrocarbons induced asphaltene precipitation, whereas the addition of CO₂ did not show such effect. Gholoum et al. (2003) compared the effects of *n*-alkanes (C1-C7) and CO₂ on the asphaltene precipitation onset point on Kuwaiti reservoir fluids and stated that in their work, CO₂ is the most effective precipitant in terms of CO₂ showing the lowest asphaltene onset pressure. According to Srivastava and Huang (1997) the most important factors which determine asphaltene precipitation during CO₂ flooding are the CO₂ concentration and the pore topography. Monger and Fu (1987) described that asphaltene deposition induced by CO₂ is comparable to the precipitation by light *n*-alkanes with a few significant differences: Asphaltene deposition induced by CO₂ is more extensive and less abrupt. The authors studied asphaltene deposition in Berea sandstone and concluded that the deposition changes the rock wettability to oil wet, regardless of the initial rock wettability. Huang (1992) believed that, depending on the asphaltene content, the wettability of Berea sandstone would change from water wet to oil wet, resulting in lower crude oil recovery efficiency. Gonzalez et al. (2007) investigated the asphaltene phase behaviour through equation of state (EoS) statistical associating fluid theory (SAFT) calculations as a function of pressure and temperature in the presence of

CO₂. They concluded that, depending on the range of pressure and temperature, CO₂ can either act as an inhibitor or precipitant for asphaltene precipitation. By applying the concept of the solubility parameter, the authors interpreted the results as follows: Below a certain crossover temperature, the solubility parameter of CO₂ is higher than the solubility parameter of the crude oil, thus leading to an increase of the asphaltene solubility in the crude oil. However, for a higher temperature the addition of CO₂ can induce asphaltene precipitation.

Due to extensive research of several authors, it can be summarised that the main parameters determining the asphaltene precipitation and deposition are temperature, pressure and oil composition, hence any change in those factors may affect the crude oil stability and provoke asphaltene precipitation. The injection of CO₂ may change the oil composition (the solubility of asphaltenes in oil) and therefore acts as a precipitant for asphaltenes. However, there is still need for research on asphaltene deposition under dynamic conditions in porous media during CO₂ flooding and on modelling asphaltene solubility in CO₂+oil mixtures.

2.3 Asphaltene Precipitation

Part of the challenge in describing asphaltene precipitation is their definition as a solubility class and not as a pure component. Three factors essentially affecting precipitation will be discussed in the beginning of the section, however only the effect of oil composition will be investigated in this thesis. Thermodynamic models predicting and describing precipitation have traditionally used the concept of the Hildebrand solubility parameter, which will be discussed in detail below. The various proposed structures have led, besides the thermodynamic approach, also to a colloidal model describing precipitation. The different views of the models on asphaltenes will be highlighted and compared thereafter. Particular focus will lie on

a predictive model, applied in Chapter 3: The UNIFAC-FV model.

2.3.1 Factors affecting Precipitation

During the recovery of crude oil, asphaltene precipitation can be affected by three main factors:

Pressure Asphaltene precipitation by a pressure change can be caused when the field pressure is above the bubble point. As an example, in the Hassi Messaoud Field in Algeria, asphaltene deposits were found on the production tubing because the wellhead pressure was near the crude oil saturation pressure, where precipitation reaches as maximum. Burke et al. (1990) investigated the solubility of asphaltenes in light crude oils (American Petroleum Institute (API) Gravity = 18 - 40) and concluded that the asphaltene solubility decreases with a decrease in pressure as long as it was above the bubble point pressure. The solubility reaches its minimum at the bubble point pressure and below the bubble point, the solubility increases with decreasing pressure.

Temperature Both Thomas et al. (1992) and Hu and Guo (2001) studied the effect of temperature on asphaltene precipitation and showed that the solubility of asphaltenes in crude oil increases with increasing temperature. However, Leontaritis (1996) stated that the change in asphaltene solubility with a change in temperature depends on the reservoir temperature: The solubility increases with temperature as long as the investigated temperature range remains below the reservoir temperature. On the other hand, when the temperature is above the reservoir temperature (for example in lab experiments), the asphaltene solubility decreases with an increase in temperature. Overall, the effect of temperature has not been well studied yet as many contradicting views are being reported in the literature.

Crude Oil Composition Asphaltene precipitation can also be caused by a change in the crude oil composition. A study by Burke et al. (1990) has shown that by an increasing amount of dissolved gas in a crude oil, the solubility of asphaltene decreases.

2.3.2 The Hildebrand Solubility Parameter

Asphaltene precipitation changes the solvent properties of the crude oil, which may happen during transport, processing and production. A parameter to estimate this phenomenon is the solubility parameter (Buckley 1999).

The Hildebrand solubility parameter δ describes the degree of solubility for non-polar or slightly polar substances without hydrogen bonding. It is defined as the square-root of the cohesive energy density (c) of the solvent and describes the amount of energy required to evaporate one unit volume of a liquid. Liquids with a similar solubility parameter are more likely to be miscible (Hildebrand and Scott 1964).

$$\delta = \sqrt{c} \quad (2.3)$$

$$c = \frac{\Delta H - RT}{V_m} \quad (2.4)$$

$$\delta = \sqrt{\frac{\Delta H - RT}{V_m}} \quad (2.5)$$

where, ΔH = heat of vaporisation, c = cohesive energy density; R = gas constant; T = temperature; V_m = molar volume

2.3.2.1 Solubility Parameter Estimation from Dilution Experiments

Due to the complex nature of crude oil, it is not straightforward to estimate the solubility parameter for crude oil. An approach to tackle that issue is through dilution experiments. The crude oil is diluted with a solvent (e.g. toluene) and a precipitant (e.g. *n*-heptane). At the precipitation onset point, a linear relationship between the added volume of solvent and precipitant is found (Figure 2.2). In the literature different definitions for the onset of asphaltene precipitation are described. For the rest of this work, the precipitation onset point is defined where the first asphaltene aggregates can be detected through filtration experiments on a filter paper.

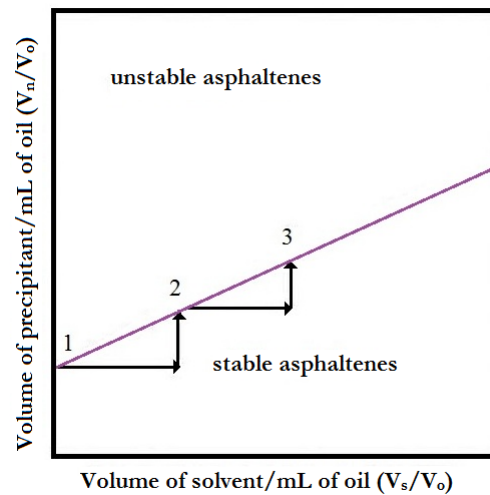


Figure 2.2: The linear relationship between solvent and precipitant volumes at the precipitation onset point.

At point 1 (Figure 2.2) the asphaltene precipitation occurs without adding any solvent $V_s = 0$ and a minimum amount V_p of precipitant. Both points 2 and 3 indicate the amount of V_s (solvent) and V_n (precipitant) needed to initiate the asphaltene aggregation. All points on the linear line define the conditions needed in order to cause asphaltene precipitation. The line distinguishes between unstable (with re-

spect to asphaltene aggregation) asphaltenes+crude oil and stable asphaltene+crude oil systems.

2.3.2.2 Solubility Parameter Estimation from Refractive Index

The refractive index (n) of a crude oil and the precipitation onset point are characteristic points for each oil sample and may vary from oil to oil. The stability of the crude oil can be estimated by measuring the refractive index of the mixture. Furthermore, the solubility parameter at the precipitation onset can be estimated (Buckley et al. 1998) and the solution properties of the crude oil can be quantified with respect to asphaltene stability. The refractive index is defined as the ratio of the speed of light in the vacuum and the speed of light in a certain medium:

$$n = \frac{c_v}{v_p} \quad (2.6)$$

where, n = refractive index; c_v = speed of light in the vacuum; v_p = speed of light in a certain medium

The solubility parameter and the refractive index are related to the van-der-Waals (v.d.W.) forces between non-polar molecules, which are responsible for precipitation. The refractive index of a mixture and pure liquids can easily be measured and the estimation of the solubility parameter becomes straightforward. For non-polar liquid hydrocarbons a linear relationship was found between the solubility parameter and the refractive index at ambient conditions (Buckley et al. 1998; Buckley and Wang 2002; Wang and Buckley 2003):

$$\delta = 52.042 \times F_n + 2.904 \quad (2.7)$$

Where F_n is defined as:

$$F_n = \frac{n^2 - 1}{n^2 + 2} \quad (2.8)$$

The linear relationship is represented in Figure 2.3.

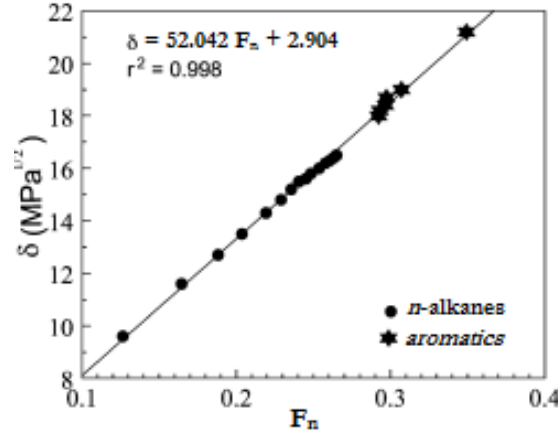


Figure 2.3: The empirical correlation between δ and F_n (Buckley and Wang 2002).

F_n and δ_{mixture} for mixtures can then be calculated, assuming a linear relationship for the volume-fraction φ of each component (Buckley and Wang 2002; Wang and Buckley 2001; Wang and Buckley 2003):

$$F_{n,\text{mixture}} = \sum_i \varphi_i F_{n,i} \quad (2.9)$$

$$\delta_{\text{mixture}} = \sum_i \varphi_i \delta_i \quad (2.10)$$

Measuring the refractive index of non-polar mixtures can therefore be used to esti-

mate the solubility parameter of the mixture.

2.3.2.3 The Solubility Parameter for Supercritical Fluids

For supercritical fluids the concept of the solubility parameter has to be extended as for fluids above their critical points, the heat of vaporisation is no longer applicable as it becomes $\Delta H = 0$ at the critical temperature. Allada (1984) has proposed a new approach by using the internal energy of the supercritical fluid relative to isothermally expanded ideal gas as the cohesive energy density. The equation by Allada (1984) can be used to estimate the solubility parameter of CO_2 at various pressures and temperatures.

$$\delta_r = \left[\frac{C_1 (E^* - E)}{R} \frac{p_r}{T_c} \frac{1}{T_r} \frac{1}{Z} \right]^{0.5} \quad (2.11)$$

$$\therefore \delta = \left[\frac{10^3 \times p_c (E^* - E) \left(\frac{p}{p_c} \right)}{RT_c Z \left(\frac{T}{T_c} \right)} \right]^{0.5} \quad (2.12)$$

where, δ_r = reduced solubility parameter ($\delta/(p_c^{0.5})$); T_r = reduced temperature (T/T_c); p_r = reduced pressure (p/p_c); E = internal energy; E^* = internal energy isothermally expanded to “zero” pressure; Z = compressibility factor; C_1 = conversion factor ($\text{cal/cm}^3 \times \text{atm}$)

2.3.3 Asphaltene Precipitation Models

Two different models for asphaltene precipitation have widely been described in the literature based on either the thermodynamic or the colloidal theory. The first one presumes that asphaltenes are part of a non-ideal mixture and precipitation occurs if the solubility falls below a certain level. Regular solution theory and EoS are

two main solubility theory approaches. The colloidal one describes asphaltenes as colloidal particles surrounded by adsorbed resins.

In all approaches the solubility power of the solvent or the oil is the most important parameter, which can be described by the Hildebrand solubility parameter. The solubility model used to describe the asphaltene precipitation is the Flory-Huggins solution theory. The chemical potential μ of the asphaltenes in the crude oil is given by Equation (2.13) (Hirschberg et al. 1984; Andersen and Speight 1999; Wang and Buckley 2001; Pazuki and Nikookar 2006):

$$\frac{\mu_a - \mu_a^\ominus}{RT} = \ln \varphi_a + \left(1 - \frac{V_{m,a}}{V_{m,s}}\right) \varphi_s + \frac{V_{m,a}}{RT} (\delta_a - \delta_s)^2 \varphi_s^2 \quad (2.13)$$

The last term in Equation (2.13) represents the Flory-Huggins interaction parameter χ :

$$\chi = \frac{V_{m,a}}{RT} (\delta_a - \delta_s)^2 \quad (2.14)$$

Hirschberg et al. (1984) simplified the above expression by assuming that the asphaltene phase is a pure liquid pseudo component, in which precipitation has no effect on the vapour-liquid equilibrium. This assumption allows for setting $\mu_a = \mu_a^\ominus$. This gives:

$$\ln \varphi_a = \left(\frac{V_{m,a}}{V_{m,s}} - 1\right) - \frac{V_{m,a}}{RT} (\delta_a - \delta_s)^2 \quad (2.15)$$

where, μ = chemical potential; $\mu^\ominus$ = chemical potential at the reference state of pure asphaltene phase; φ = volume fraction; δ = solubility parameter; V_m = molar volume. The subscripts a and s denote asphaltenes and solvent containing all nonasphaltene components, respectively.

Equation (2.15) can be used to calculate the maximum volume fraction of asphaltenes soluble in the crude oil.

2.3.3.1 Colloidal Model

It has been hypothesized since 1920 that asphaltenes exist in a colloidal phase and are dispersed insoluble in the oil. In this model idea, asphaltenes are surrounded by resins with lower molecular weight and less aromatic nature. The resins stabilise the asphaltenes by adsorbing on to their surface and their partitioning between the surface and surroundings determines the asphaltene solubility. Destabilisation and precipitation can therefore occur due to a shortage of resins (Buenrostro-Gonzalez et al. 2004). This model predicts that precipitation is irreversible. The assumption of the model is that the dissolved resins are in equilibrium with the adsorbed resins on the asphaltene molecule:

$$\mu_{r,0} = \mu_{r,m} \quad (2.16)$$

where, $\mu_{r,0}$ = chemical potential of the resins in the crude oil; $\mu_{r,m}$ = chemical potential of the resins adsorbed on the asphaltenes

If the resins are considered to be similar to monodisperse polymers, then the Flory-Huggins solution theory can be applied to define the volume fraction φ_r of the resins:

$$\ln \varphi_r = \frac{V_{m,r}}{V_{m,s}} - \frac{V_{m,r}}{RT}(\delta_r - \delta_s)^2 - 1 \quad (2.17)$$

where, φ_r = resin volume fraction; δ_r = solubility parameter of the resins; $V_{m,r}$ = molar volume of the resins

$\varphi_{r,c}$ is known as the critical resin concentration in the crude oil and depends on temperature, pressure, oil composition and solubility. If $\varphi_r > \varphi_{r,c}$ then the asphaltenes

don't precipitate and the system is considered to be stable. However, if $\varphi_r < \varphi_{r,c}$ then the asphaltene precipitate. Therefore, the stability of the asphaltenes depend on a certain resin to asphaltene ratio, which, according to Koots and Speight (1975), is 1.25. However, it is known that the Hassi Messaoud crude oil (South Algeria) has a resin-to-asphaltene ratio of 22 and yet asphaltene precipitation problems were reported (Minssieux et al. 1998). If light alkanes are added to the system, the solution is a better solvent for the resins and they dissociate from the asphaltene, initiating asphaltene precipitation (Porte et al. 2003). Sheu and Storm (1995) measured that the addition of maltenes prevents precipitation of the asphaltenes. This suggests that maltenes act as stabilisers for the aggregates and also shift the mixture solubility parameter.

Limitations of the Flory-Huggins Theory The Flory-Huggins theory has been applied to describe the thermodynamics of polymer solutions and to approximate the ideal polymer solution behaviour to that of a real solution. Examples are comparing liquid-liquid phase behaviour of a polystyrene + cyclohexane system to experimentally obtained phase curves (Saeki et al. 1974). However, several limitations of the Flory-Huggins theory exists due to a number of assumptions made, such as: The Flory-Huggins interaction parameter χ is assumed to be independent of temperature and concentration of the solute in the solvent, however some examples have shown that this assumption is incorrect (Danner and High 1993). No change in volume is assumed to occur upon mixing of a higher molecular weight solute and the solvent and it treats the mixture as being incompressible. The first major change to address the issue of compressibility was made in 1976 by Sanchez and Lacombe by incorporating the compressibility into the derivation of the Gibbs free energy of mixing, which is now known as the Sanchez-Lacombe equation of state model. The Flory-Huggins theory assumed a rigid lattice which does not allow for density

changes, as well as having lattices occupied by either solvent or polymer molecules, where Sanchez and Lacombe (1978) allowed the existence of vacancies in their lattice model. They have found good agreement in comparing calculated and experimental data of enthalpy changes for a poly(isobutylene)solution (Danner and High 1993).

2.3.3.2 Thermodynamic Model

Kokal et al. (1992) suggested that asphaltenes are dissolved in crude oil and depending on thermodynamic conditions, they can precipitate. In this approach, resins are not taken into account and precipitation can be reversed. Reducing the asphaltene solubility can lead to phase separation. Asphaltenes can then remain in the asphaltene-poor lighter phase (phase L) and others in an asphaltene-rich phase (phase H). At thermodynamic equilibrium, the chemical potentials for each component are equal in both phases (Wang and Buckley 2001):

$$\begin{aligned}\Delta\mu_s^L &= \Delta\mu_s^H \\ \Delta\mu_a^L &= \Delta\mu_a^H\end{aligned}\tag{2.18}$$

Generally two model classes are considered when using the thermodynamic model approach to describe asphaltene precipitation:

Equation of State (EoS) Model EoS models are used to relate pressure to temperature to predict phase behaviour of hydrocarbons and asphaltenes. This model assumes that all asphaltenes in the crude oil have the same size and molecular weight. Attempts have been made to use the EoS models to predict asphaltene phase behaviour by Akbarzadeh et al. (2002).

Activity Coefficients Model (ACM) The alternative to EoS models are activity coefficient models (ACM), which assume that precipitated asphaltenes do not affect the vapour liquid equilibrium (VLE). These models are used to predict the activity coefficient γ in a mixture. The activity coefficient γ_i describes the deviation from ideal behaviour presented in Raoult's law, for which $\gamma = 1$. The general expression for determining γ_i is:

$$\gamma_i = \left(\frac{y_i}{x_i} \right) \left(\frac{p}{p_i^\sigma} \right) \left(\frac{\Phi_i^v}{\Phi_i^\sigma} \right) \left(\frac{1}{F_i} \right) \quad (2.19)$$

where, y_i and x_i = mole fractions of components i in the vapour and liquid phase, respectively; p_i^σ = saturated pressure of pure component i ; Φ_i^v = fugacity coefficient of component i in the vapour-phase composition; Φ_i^σ = fugacity coefficient of the pure saturated vapour; F_i = Poynting factor

At low pressure, the third term approximates the behaviour of an ideal gas as: $\Phi_i^v = \Phi_i^\sigma$ and the Poynting factor becomes negligible.

One approach to calculate the ACM parameters is through a group contribution method. Here the mixture is considered to consist of the structural unit (sub-groups) of the components present in the mixture, rather than being considered as molecules making the components. The activity coefficients are dependent on both the properties of each sub-group and the interaction among them. Similar sub-groups can then be assigned to a main group which are then considered to be identical with respect to their group interactions (García Sakai 2002).

2.3.3.3 Universal Functional-Group Activity Coefficients with Free Volume (UNIFAC-FV) Model

An example based on group-contribution is the predictive model UNIFAC-FV (Oishi and Prausnitz 1978), which was specifically derived for polymer+solvent mixtures. Due to its predictive capability, several modifications were made to extend its ap-

plication to a wide range of temperature and pressure. Limitations of these models, however, were discovered in the region of critical temperature and pressure. The critical points cannot exactly be determined because different phases require a different physical model. The activity coefficients are calculated at temperatures being equal to the temperature of the mixture, which would mean that the pure components are in its liquid state. Even though, the UNIFAC-FV model yields accurate predictions, it may become unreliable in highly diluted regions for non-diluted systems (Danner and High 1993).

In the UNIFAC models the activity a of a component in a mixture is calculated from two contributions, accounting for differences in molecular sizes and an residual or energetic contribution due to molecular interactions. UNIFAC has proven to be a well known and widely used technique to calculate activities in systems containing small molecules, however it has difficulties accounting for macromolecules. Therefore, Oishi and Prausnitz (1978) introduced a contribution term (free-volume term) accounting for size differences: UNIFAC-FV. The UNIFAC-FV by Oishi and Prausnitz is currently the most accurate method to predict solvent activities in polymers (Danner and High 1993). The activity coefficient can be calculated as follows:

$$\ln\gamma_i = \ln\gamma_i^{\text{comb}} + \ln\gamma_i^{\text{res}} + \ln\gamma_i^{\text{FV}} \quad (2.20)$$

The contributions are the combinatorial expression (comb), the residual term (res) and the free-volume term (FV). The combinatorial term is defined as:

$$\ln\gamma_i^{\text{comb}} = \ln\frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} - \frac{z}{2} \left(\ln\frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right) \quad (2.21)$$

where, z = coordination number, set to 10; ϕ_i = molecular volume fraction of component i ; θ_i = molecular surface fraction of component i

where:

$$\phi_i = \frac{x_i r_i}{\sum_j^{nc} x_j r_j} \quad \text{and} \quad \theta_i = \frac{x_i \frac{z}{2} q_i}{\sum_j^{nc} x_j \frac{z}{2} q_j} \quad (2.22)$$

where, nc = number of components in the mixture; r_i = volume parameter of molecule i ; q_i = surface parameter of molecule i

where:

$$r_i = \sum_k^{ng} v_{ki} R_k \quad \text{and} \quad q_i = \sum_k^{ng} v_{ki} Q_k \quad (2.23)$$

where, ng = number of groups in the mixture; v_{ki} = number of groups of type k in molecule i ; R_k = volume parameter for group k ; Q_k = surface parameter for group k

The residual term is defined as follows:

$$\ln \gamma_i^{\text{res}} = \sum_k^{ng} v_{ki} [\ln \Gamma_k - \ln \Gamma_k^i] \quad (2.24)$$

where, Γ_k = residual activity coefficient of group k ; Γ_k^i = residual activity coefficient of group k in a mixture of groups corresponding to the pure component i

The parameters Γ_k and Γ_k^i are defined as per below:

$$\ln \Gamma_k = Q_k \left(1 - \ln \sum_m^{ng} \theta_m \tau_{mk} - \sum_m^{ng} \left(\frac{\theta_m \tau_{km}}{\sum_n^{ng} \theta_n \tau_{nm}} \right) \right) \quad (2.25)$$

where:

$$\theta_k = \frac{X_k \frac{z}{2} Q_k}{\sum_m^{ng} X_m \frac{z}{2} Q_m} \quad \text{and} \quad \tau_{mk} = e^{-b_{mk}/T} \quad \text{with} \quad X_k = \frac{\sum_j^{nc} v_{kj} x_j}{\sum_j^{nc} \sum_m^{ng} v_{mj} x_j} \quad (2.26)$$

where, τ_{mk} = interaction parameter for group m with group k ; θ_m = group surface area fraction

of group m ; b_{mk} = interaction parameter for group m with group k ; X_k = group mole fraction of group k

The free-volume contribution was defined as follows:

$$\ln \gamma_i^{\text{FV}} = 3C_i \ln \left[\frac{\tilde{V}_i^{1/3} - 1}{\tilde{V}_m^{1/3} - 1} \right] - C_i \left[\left(\frac{\tilde{V}_i}{\tilde{V}_m} - 1 \right) \left(1 - \tilde{V}_i^{1/3} \right)^{-1} \right] \quad (2.27)$$

where:

$$\tilde{V}_i = \frac{V_i}{0.01517br_i} \quad \text{and} \quad \tilde{V}_m = \frac{\sum V_i x_i}{0.01517b \sum r_i x_i} \quad (2.28)$$

where, C_i = external degree of freedom parameter, 1.1 for solvents; $b = 1.28$; r_i = volume parameter for component i ; $\tilde{V}_i$ = reduced volume of component i ; calculated from Tait equation for polymers.

From an experimental point of view, it is desirable to investigate a full set of thermodynamic conditions at which asphaltene precipitation for an individual oil occurs. However, due to the complex nature of the hydrocarbon mixture, this is impractical and difficult. Therefore, thermodynamic models are used with a minimum of laboratory data to predict the precipitation behaviour. A simple approach is to treat asphaltenes as a separate component and as asphaltenes are the heaviest components in the crude oil, thermodynamic models accounting for large molecules (e.g. polymers) with smaller solvent molecules are usually used. Usually polystyrene (PS) is chosen to represent asphaltenes, if one would neglect the heteroatoms, as they share structural similarities such as their size, the aromaticity and alkyl chains and the interaction occurs mainly through dispersion forces. In crude oil, asphaltenes exist as polydisperse components, however, for the sake of simplicity, polystyrene is generally modelled as a monodisperse molecule. Using PS as a model component to

represent the asphaltenes is not a new idea: Vargas et al. (2009) modelled the phase behaviour of a PS, cyclohexane and CO₂ mixture and showed similarities to experimental phase behaviour studies of asphaltenes in crude oil. Artola et al. (2011) calculated a constant composition p - T phase diagram showing the bubble curve and asphaltene precipitation boundary due to liquid-liquid phase separation, using PS as an oligomer or polymer with different molecular weight.

2.4 Asphaltene Deposition

Asphaltene deposition refers to the process when asphaltene aggregates attach to a surface. Depending on the interaction between surface and asphaltenes they may adsorb on the surface (Alian et al., 2011).

Studies of asphaltene deposition are mainly conducted in three ways: In microfluidics (more specifically capillary flow), in Taylor-Couette (TC) cells or in core-flooding experiment through a porous media. Selected literature about asphaltene deposition studies will be presented below. The section concludes with an introduction to X-Ray Microtomography; an imaging technique whose potential to image asphaltene deposits in porous media will be shown in Chapter 5.

2.4.1 Microfluidic Experiments

The use of microfluidic devices over the past 15 years has opened new possibilities in studying fluid mechanics and discovering new physical phenomena. As the dimension of the equipment shrinks, the bulk properties of the fluid become less important and interfacial properties and fluid-solid interactions dominate. Microfluidic studies offer new and interesting possibilities to researchers and the potential to study effects, such as colloidal dynamics at low Reynolds (Re) numbers, where the small dimension of the capillary or the microfluidic device offers the suitable length scale (Saha and

Mitra 2012).

2.4.1.1 Asphaltene Deposition in Capillary Flow

Wang et al. (2004) studied asphaltene deposition in a stainless steel capillary for two different crude oils and reported a higher deposition rate with higher molecular weight precipitants (*n*-pentadecane) than with lower molecular weight components (*n*-heptane). They assumed that the dead oil samples already contained precipitated asphaltenes which did not deposit on the capillary walls and were more likely entrained with the flow. In their work, an influence of the flow rate on the deposition rate was not found.

Boek et al. (2008) investigated asphaltene deposition in a glass capillary. The experimental results were compared and evaluated with stochastic rotation dynamics (SRD) simulations. Further information about SRD are given in Section 2.5.1. The asphaltenes were precipitated from the crude oil with *n*-heptane at a crude oil:precipitant ratio 1:40 and then redissolved in toluene, to keep the asphaltene concentration at 1 g/L. Boek et al. (2008) investigated the effect of two different total flow rates $Q_t = 5 \mu\text{L}/\text{min}$ and $10 \mu\text{L}/\text{min}$. The injection ratio of *n*-heptane to the asphaltene+toluene mixture was set to 60:40. The fluids were co-injected through a glass capillary and the pressure drop was measured as a function of time. Simultaneously, images of the capillary and the deposited asphaltenes were taken with an optical microscope. The increasing pressure drop observed over time was attributed to the asphaltene deposition on the capillary walls and increased with increasing Q_t . The experiments were repeated three times and for all experiments different deposition rates were observed. For some experiments, the deposition was followed by an erosion of asphaltenes due to bigger flocs present in the flow. A similar observation was obtained from the simulations carried out, in which the potential well depth ε_{a-a} and the flow rate were varied to obtain $Pe^{\text{flow}} \gg 1$ and

$Re \ll 1$. It was found that with increasing well depth the asphaltenes become more “sticky”, leading to a blockage of the capillary ($\varepsilon_{a-a} = 10 - 20 k_B T$). Boek et al. (2008) investigated asphaltene deposition in a glass capillary, as glass represents a sandstone reservoir rock reasonably well. On the contrary, Wang et al. (2004) used a stainless steel capillary, which is a closer representation of process tubing.

In a following work, Boek et al. (2010) studied the deposition in capillary flow of asphaltenes precipitated from the whole crude oil. The experimental set-up and conditions remained the same as in the previous work. For the higher flow rate they observed a deposition-erosion/entrainment cycle, as well as higher pressure fluctuations when compared to experiments at lower flow rate. By comparing the dimensionless conductivity, Boek et al. (2008) and Boek et al. (2010) concluded that the precipitated, extracted asphaltenes are “stickier” than asphaltenes from the whole crude oil.

Broseta et al. (2000) investigated the onset point and deposition rate as a function of pressure, temperature and different fluid compositions. They measured the pressure drop over the length of a stainless steel capillary, into which the fluids were injected at a constant flow rate. Similar to other workers, they measured a pressure increase due to the build-up of the deposited layer of asphaltenes. According to Broseta et al. (2000), the asphaltenes precipitated when the mixture contained enough n -alkane to destabilise the asphaltenes in the crude oil. The hydrodynamic thickness of a deposited asphaltene layer was calculated, assuming that the asphaltenes formed a uniform layer on the capillary wall. However, Boek et al. (2008) believed that such an assumption may not be justified, because they found that the amount of asphaltenes deposited decreases along the length of the capillary.

Lawal et al. (2012) extended the work of Boek et al. (2008) and Boek et al. (2010) to the comparison of different precipitants. Asphaltenes, in a toluene diluted oil sample, were precipitated with different n -alkanes and it was found that a precipitant

with a lower carbon number led to an increase in the deposition rate.

Hoepfner et al. (2013) initiated asphaltene precipitation and deposition by co-injecting *n*-heptane and crude oil through a metal capillary and stated that asphaltene aggregates larger than 0.5 μm do not deposit on the wall of the capillary. By imaging the capillary with electron microscopy they also found a non-uniform axial deposition profile.

The Homogeneous Deposition Model Broseta et al. (2000), Wang et al. (2004) and Lawal et al. (2012) have proposed a model to calculate the effective hydrodynamic thickness of a layer of deposited asphaltenes, assuming a homogeneous layer of deposits. The experimental pressure drop data was used to estimate the deposit layer of the asphaltenes by the change of the inner diameter of the capillary. The model is based on the assumption of a homogeneous deposition with a uniform thickness of the asphaltene deposit layer. For a constant Poiseuille flow the following expression can be applied:

$$\frac{(\Delta p_t)r_t^4}{\mu_t} = \frac{(\Delta p_i)r_i^4}{\mu_i} \quad (2.29)$$

where, Δp_i = pressure drop across the capillary before precipitation; Δp_t = pressure drop across the capillary at time t ; r_i = initial tube radius; r_t = effective tube radius after precipitation and deposition

To minimize the error caused by pressure fluctuations, the Hagen-Poiseuille equation is used to calculate Δp_i :

$$\Delta p_i = \frac{128\mu_i L Q_t}{\pi d_H^4} \quad (2.30)$$

Assuming that the change in the viscosity can be neglected ($\mu_t = \mu_i$), the equation can be rearranged to:

$$r_t = r_i \left(\frac{\Delta p_i}{\Delta p_t} \right)^{1/4} \quad (2.31)$$

The radius r_t is related to the asphaltene deposit hydrodynamic thickness e_t .

$$r_t = r_i - e_t \quad (2.32)$$

Therefore, e_t can be estimated from the following equation:

$$e_t = r_i \left[1 - \left(\frac{\Delta p_i}{\Delta p_t} \right)^{1/4} \right] \quad (2.33)$$

2.4.2 Taylor Couette (TC) Device Studies

The advantage of studying deposition in TC cells is that they can be operated at reservoir pressure and temperature. By varying the flow rate, the shear rate can be changed and the deposit mass growth can be measured over time (Buckley 2012). Eskin et al. (2011) studied asphaltene deposition in a Couette device during turbulent flow as observed in production tubing. Primary asphaltene particles deposited from the crude oil at a pressure which lies below the *asphaltene precipitation onset pressure*, followed by aggregation driven by Brownian motion and turbulent disper-

sion. Depending on the aggregate size the asphaltenes were able to deposit on the wall. Based on that observation, they introduced the concept of the critical particle size, describing an equilibrium between v.d.W. forces and viscous drag forces. However, particles which were larger than the critical particle size did not deposit, meaning that deposition is a limiting process once the aggregates have reached the critical particle size. They observed a decrease in the deposition rate for a higher shear rate. Based upon this observation, Eskin et al. (2011) developed a population balance model which predicts the transport of the particles.

Asphaltene Aggregation in Couette Flow Experiments to measure asphaltene floc size distribution have been carried out by Rahmani et al. (2003), where aggregation and fragmentation of asphaltenes were studied in a Couette device for an Athabasca bitumen as a function of shear rate. The diameter of the inner cylinder in the Couette reactor was 50 mm and the outer cylinder had a diameter of 60 mm, giving an annular gap of 5 mm. C7-asphaltenes were re-dissolved in toluene and imaged with a charged-coupled device (CCD) camera to measure the floc size as a function of time at a constant shear rate in the range $1.2 - 12.7 \text{ s}^{-1}$. Their experiments revealed that the average asphaltene aggregate size increases up to a given maximum size, followed then by a decrease in mean size until reaching a steady-state which corresponds to a balance between aggregation and floc break up. Due to the limited optical resolution, aggregate sizes smaller than $30 \text{ }\mu\text{m}$ were not detected.

According to Rahmani et al. (2003), the particle aggregation rate depends on the collision frequency and on the sticking probability. They state that, on the other hand, fragmentation is not yet well understood and for that purpose they established a population balance. During the initial stages of shear-induced aggregation the floc size increases until the hydrodynamic forces acting on the aggregate approach the value for its yield stress, resulting in a continuous floc break up. The rate of change

of average floc size can be modelled with the following equation:

$$\frac{dn_i}{dt} = 0.5 \sum_{j+k=i} \alpha \beta_{jk}(V_j, V_k) n_j n_k - n_i \sum_{k=1}^{n_{\max}} \alpha \beta_{ki}(V_k, V_i) n_k - B_i n_i + \sum_{j=i+1}^{n_{\max}} \gamma_{i,j} B_j n_j \quad (2.34)$$

where, n_i = number concentration of flocs with size i ; α = collision efficiency; β_{jk} = collision frequency for particles of volume V_j and V_k ; B_i = break up rate of flocs with size i ; $\gamma_{i,j}$ = break up distribution function defining volume fraction for flocs of size i originating from flocs with size j .

The first term describes the formation of particles with size i by collision of j and k -sized particles. In the second term, the loss of particles with size i by collisions with any other particle is described, the third term highlights the loss of particles with size i due to break up and the last term states that particles with size i get formed due to break up of larger flocs.

2.4.3 Porous Media Studies

Numerous studies have focused on studying asphaltene deposition in absence of porous media. Hence the applicability of these studies may be limited to deposition problems in production tubing. However, production tubing is more easy accessible to cleaning by solvents. Asphaltene deposition problems encountered deep down in rock reservoirs is equally problematic, but much more challenging to tackle.

The work by Minssieux (1997) was one of the first studies where asphaltene deposition in porous media was extensively studied. In core-flooding experiments, various core samples with different rock characteristics were studied ($k = 0.67$ - 107 mD and $\phi = 7.1$ - 24.7%). The asphaltene content in the dead oil samples, used in this experiment, varied from 0.15 - 5.3 wt%. The core-flooding experiments were conducted at two different temperatures of $T = 323$ and 353 K and the back

pressure was set to 10 bar. The oil samples were injected through the rock samples with flow rates in the range of 5 - 80 cm³/h and the damage caused by asphaltene deposition in the rock sample was quantified through a change in pressure drop across the length of the sample. Minssieux (1997) concluded that plugging of the porous sample was observed only after a sufficient amount of oil has flown through the sample and that damage at earlier times was only observed in samples with a lower initial permeability.

Jafari Behbahani et al. (2013) developed a new model based on multilayer adsorption kinetics and validated the results through experimental determination of permeability reduction in several rock samples from a Iranian bottom hole live oil. The new model aimed to distinguish between mechanical plugging and surface adsorption. The experiments have shown that an increase in oil injecting flow rate results in a higher permeability reduction and that 60-80% of the damage done due to deposition is caused by plugging.

Pak et al. (2011) studied asphaltene deposition in a coreholder containing a sandstone, in which asphaltene deposition was assessed through pressure drop measurements across the vessel. The amount of deposited asphaltenes within the core was evaluated through the difference of asphaltene content in the inlet and outlet stream. This indirect method was applied to study asphaltene deposition caused by three different processes: Recycled gas injection, CO₂ injection and natural depletion. According to Pak et al. (2011), recycled gas injection caused the most significant damage and natural depletion resulted in the least. They have also observed that porosity reduction occurred mostly in the core inlet.

Similarly, Papadimitriou et al. (2007) studied asphaltene deposition in porous media and they concluded that asphaltene deposits may get entrained back into the flow. Thus, actually permeability will vary with respect to time, furthermore taking into account that absolute blockage of a sample has barely been encountered.

A combined theoretical and experimental study was carried out by Mendoza De La Cruz et al. (2009). In the model, the porous medium was represented as a network of pore bodies joined together by pore throats. Permeability reduction was assumed to have occurred due to two main mechanisms: *(i)* The asphaltene deposits are significantly smaller than the size of pores and throats, leading to a gradual reduction of pore throat radii and *(ii)* the deposition of aggregates are larger than the size of a given throat, hence leading to a reduction in the fluid flow area. However, it should be noted that the model by Mendoza De La Cruz et al. (2009) does not account for entrainment of particles, thus failing to describe the deposition process under dynamic conditions. The model was used to validate core-flooding experiments, which have shown that asphaltene precipitation and deposition reduced both initial oil permeability and effective porosity by 24% and 20%, respectively, as the pressure is reduced until near the bubble point pressure.

The Colloidal Approach Nabzar and Aguiléra (2008) studied the deposition kinetics in capillary flow and core-flood experiments of ideal and real systems above the precipitation onset point as a function of flow rate to verify that the classical laws for colloidal deposition, based on the the theory of colloid transport and deposition in porous media, can be applied to describe asphaltene deposition in porous media. The authors state that above a threshold value of shear the deposition rate decreases due to entrainment or detachment limiting multilayer deposition. They identified three deposition regimes: At low shear rates the deposition is **diffusion-controlled** and beyond a certain critical shear rate the regime is called **shear-limited** deposition. Beyond another critical shear rate, the deposition is independent of the flow rate. Both critical shear rates increase with increasing asphaltene instability, i.e. increasing precipitant fraction. According to Nabzar and Aguiléra (2008), increasing precipitant fraction perhaps increases asphaltene-asphaltene interaction and there-

fore the shear rate needed to break up the flocs and thus their adhesion to the surface.

2.4.4 Imaging of Asphaltenes

2.4.4.1 X-Ray Computed Microtomography

X-Ray computed tomography (CT) is a relatively new technique in petroleum engineering to observe single and multiphase fluid flow in porous medium and to characterise the reservoir rock (heterogeneity or homogeneity, deposits and fractures). The advantage of X-Ray computed tomography is its wide application range. It reveals compositional changes within the structure and allows for studying porosity and saturation without altering either fluids or rock properties. The fundamental of CT imaging is that X-Rays pass through almost all substances and the resulting projection images can be reconstructed into 3D images, where the small volume elements in that images are called voxels. The grey scale intensity in each voxel corresponds to the attenuation in that volume.

The intensity of each voxel can be related to the X-Ray attenuation. X-Rays can either be absorbed or scattered at a volume point in the sample. The linear attenuation can be described with the Lambert-Beer law:

$$I = I_0 \exp(-\epsilon L) \quad (2.35)$$

where, I = transmitted intensity; I_0 = initial intensity; ϵ = linear attenuation coefficient; L = optical length through the sample

The linear attenuation is mainly a function three parameters: *(i)* the material density, *(ii)* its atomic number and *(iii)* the X-Ray beam energy. The ratio I/I_0 then describes the degree of attenuation of X-Rays passing through the sample.

The basic components of a X-Ray CT scanner are the X-Ray source, a rotation system and a detector. The configuration used depends on both the sample size and the desired resolution. Table 2.1 summarizes the different classes of X-Ray computed tomography.

Table 2.1: General classification of X-Ray computed tomography (Mees et al. 2003).

Type	Scale of Observation	Scale of Resolution
Medical	m	mm
High-resolution	dm	100 μm
Ultra-high-resolution	cm	10 μm
Microtomography	mm	μm

In comparison to medical CT, a much higher resolution is achieved using Microtomography (microCT). X-Rays penetrate into the object and create a volumetric (3D) representation of the object. Back projection algorithms then reconstruct the images as a stack of 2D slices, without destroying the original sample.

With microCT, the total porosity of reservoir rock, such as sandstones, can be measured, regardless of the connectivity (Mees et al. 2003). Using microCT, the pore network can be extracted whilst preserving the topology of the pore space.

2.4.4.2 Imaging of Core-flood Experiments

Knackstedt et al. (2011) imaged and studied the pore scale crude oil brine populations to quantify the residual oil phase and to estimate wettability alteration. For that purpose, several imaging techniques were applied, such as surface chemical techniques (SEM and SEM-EDS) and X-Ray microCT. Using microCT, 3D images were obtained with a voxel size down to ~ 1.5 μm resolution. All images were composed of 2048^3 voxels. The samples (both cleaned and after injection of hydrocarbons) were scanned at varying scales using different imaging modes and functional agents to dope the hydrocarbon phase. Figure 2.4 shows an example of a slice through a

carbonate core plug. Knackstedt et al. (2011) concluded that regions, which are rich in hydrocarbons, are mainly mesoporous.

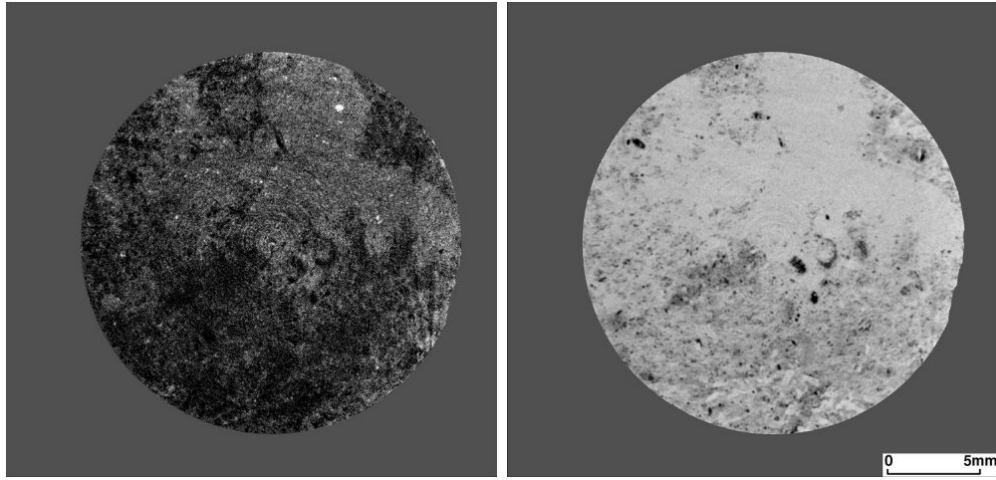


Figure 2.4: Comparison of a core plug with residual hydrocarbons (left) and the cleaned plug (right). *The brighter regions in the left image indicate the presence of residual hydrocarbons. The scan of the cleaned plug emphasizes the pore structure → The darker regions are more porous* (Knackstedt et al. 2011).

Srivastava et al. (1999) investigated asphaltene deposition in the Weyburn reservoir by performing experiments at reservoir conditions. The deposition process was studied as a function of CO_2 concentration, operating pressure, and formation brine through dynamic core-flood experiments and microCT. They detected an increase of asphaltene deposition in the core matrix due to CO_2 injection (flow rate = $2 \text{ cm}^3/\text{h}$), as well as a significant amount of deposition occurring near the core inlet. The core was scanned before the experiment (→ clean core matrix) and after conducting the experiment (→ matrix containing precipitated asphaltenes). Both scans were obtained at the same part of the core at intervals of 1 cm along the core length (Figure 2.5a and Figure 2.5b).

The overall length of the core was 23 cm and imaged at 22 different core locations. The first image in Figure 2.5a and Figure 2.5b represents the location near the core inlet (approximately 0.5 cm). The image at the bottom right represents the scan

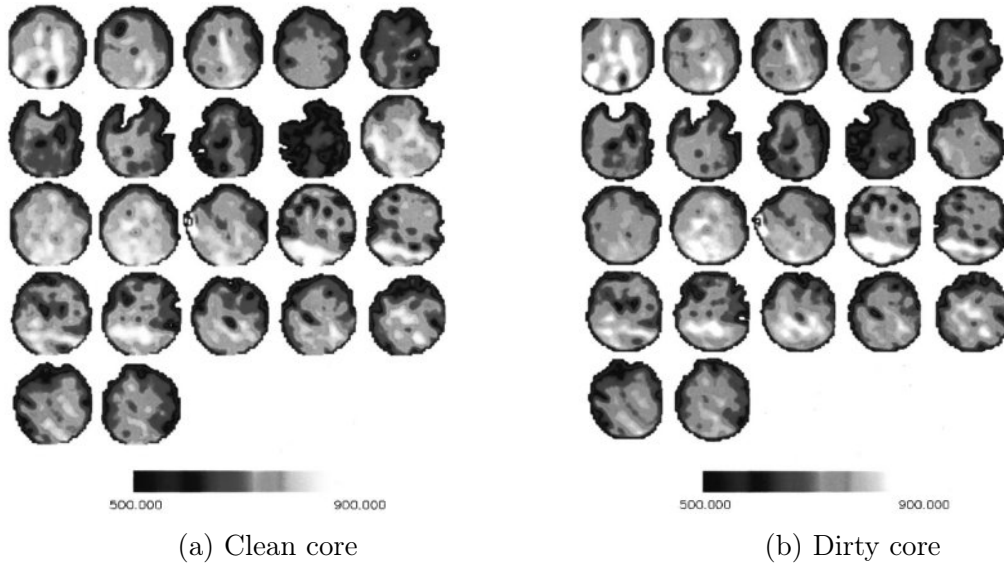


Figure 2.5: MicroCT images of the clean core and dirty core at 1 cm intervals along the core length. Top left $\rightarrow$ right (Srivastava et al. 1999).

closest to the core outlet. The highest density (CT Number = 900) is represented by the white parts in the images and the lowest by black (CT Number = 500). The grey shades show an intermediate matrix grain density. Srivastava et al. (1999) observed that the high density areas increased in the dirty core and attributed this to asphaltene precipitation/deposition. Srivastava et al. (1999) showed the capability of X-Ray imaging for visualizing the core matrix, however, difficulties occurred in determining the exact location of deposited asphaltenes.

2.5 Computational Modelling

Modelling hydrodynamics of complex fluids such as colloidal suspensions can be non-trivial, as both short-term Brownian motion and long-term hydrodynamics of the solvent come into effect. The difficulties become apparent when considering the large time- and length scales differences between microscopic solvent particles and mesoscopic colloids, hence coarse-graining becomes necessary. For these type

of simulations, the mesoscopic methods often seem more efficient than conventional fluid dynamics simulations. Therefore, lattice-gas based techniques have been stimulated to resolve the Navier-Stokes equations, such as lattice gas automata (LGA) and lattice-Boltzmann (LB) methods which are very efficient due to simplified collision dynamics. These methods have the advantage that only a few conditions, such as energy and momentum conservation, have to be met. However, according to Ihle and Kroll (2001), LB can suffer from numerical instabilities. Recently, particle based mesoscopic simulations such as dissipative particle dynamics (DPD) have therefore been developed in order to couple solids and solvent in a different way, which do not experience these drawbacks such as the lattice based methods, but they can, however, be complex and difficult to analyse analytically. A promising particle-based method is stochastic rotation dynamics (SRD), where the particles move in a continuous space and generating the correct Navier-Stokes hydrodynamics as long as momentum and energy are being conserved. According to (Padding and Louis 2006), SRD becomes more efficient when complex particles in a solvent requires simulating.

The LB and SRD methods are further described in the following section, along with a selected continuum model; the Deep Bed Filtration (DBF) model. The DBF model and LB calculations will be used to assess permeability damage due to asphaltene deposition in a reservoir rock (Chapter 5) and with the SRD method fractional deposition in a capillary will be related to the applied body force (Chapter 4).

2.5.1 Mesoscale Simulation Methods

In general, two computational models can be applied to model fluid dynamics: (i) the particle model which is suitable for the microscale and (ii) the continuum model which addresses simulation at the macroscale. Due to the challenge of traditional

methods to model complex fluids, such as coupling the continuous and discrete approaches, several mesoscale models have been developed over the last years. Figure 2.6 summarises the two traditional models (particle model and continuum model) for the microscale and macroscale. At the mesoscale, the mesoscopic algorithms can be applied.

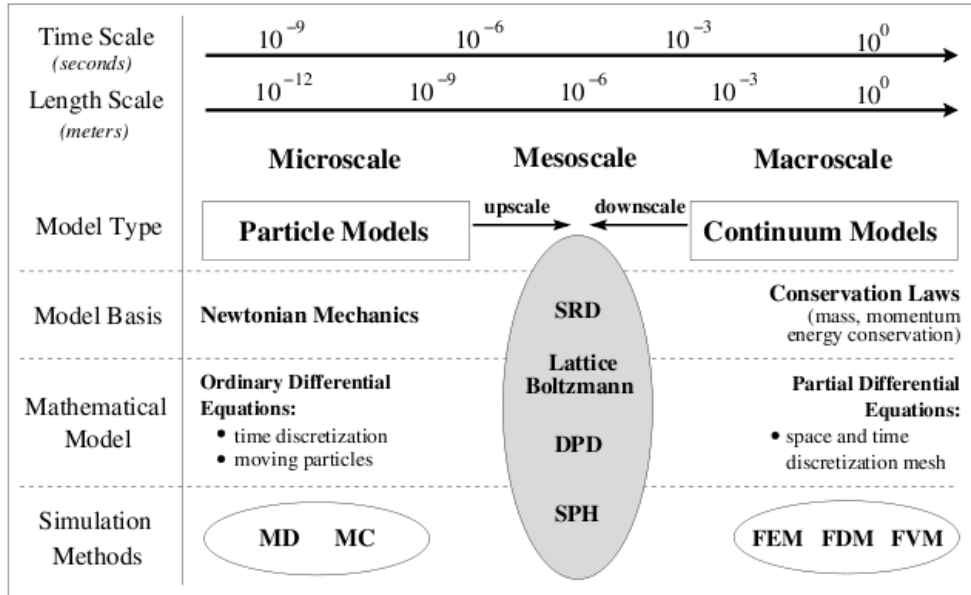


Figure 2.6: Comparison of the different methods to model fluid behaviour (Microscale, Mesoscale and Macroscale) including the time and length scale, where they can be applied. *MD* = *Molecular Dynamics*; *MC* = *Monte Carlo*; *DPD* = *Dissipative particle dynamics*; *SPH* = *Smoothed-particle hydrodynamics*; *FEM* = *Finite element method*; *FDM* = *Finite difference method*; *FVM* = *Finite volume method*

It can be distinguished between two different approaches: In the **lattice-based methods**, the LB method is used to provide a finite difference solution of the Navier-Stokes equation. The second group (**particle-based methods**) is represented by SRD, which will be discussed later.

2.5.2 Deep Bed Filtration (DBF) Models

Asphaltene formation damage can be described by so called Deep Bed Filtration (DBF) models. In the past, DBF models were primarily used to describe damage caused by solid precipitates or solid suspended particles on an internal filter bed (Lawal et al. 2011). During the particulate suspension flow through a porous medium, a separation between the solid phase and the liquid phase of the suspension can occur. The retention process of particles is known as Deep Bed Filtration, which can occur due to several mechanisms: Contact between the particles and the retention site, fixing of particle sites and finally the break off of formerly retained particles (Fallah et al. 2012). The DBF models describe the particles as a concentration field, using equations for flow continuity, mass balance and kinetics. Early work on reviewing the DBF model was done by Hertzog et al. (1970) where two types of deep filtration were defined: A mechanical filtration for larger particles ($d > 30 \mu\text{m}$) and a physiochemical filtration for smaller particles ($3 \mu\text{m} < d < 30 \mu\text{m}$). Boek et al. (2012) developed a DBF model to estimate the effects of particle trapping from drilling fluids on formation damage, i.e. the change in the permeability. For this type of model, the macroscopic approach was used since it was assumed that the invading particles are much smaller than the pore throats. Lawal et al. (2011) investigated the permeability change in porous media due to asphaltene deposition and incorporated it into the DBF theory. They developed parameters that account for precipitation, aggregation, deposition and hydraulic behaviour of the porous medium. Lawal et al. (2011) described deposition as a homogeneous filter bed through which asphaltenes can pass through where precipitation was assumed to be irreversible. Based on mechanisms, such as sedimentation, adsorption and aggregation, a differential equation was proposed to approximate the deposition rate. The model was validated against experimental data and has shown good agreement with

regards to permeability reduction. Experimental studies about *in-situ* upgrading on heavy oil by catalytic hydrogenation using a dispersed catalyst in the submicrometer region were conducted by Zamani et al. (2010). The dispersed catalysts are transported through porous media in order to accelerate high-temperature upgrading reactions. Zamani et al. (2010) have successfully shown that the catalyst suspension can be propagated through sand beds with, however, a few catalyst particles being retained by the sand. The particles deposited on the sand, which was found to be almost irreversible. Nanodispersed catalysts were propagated through the sand, but larger aggregated particles were filtered out, thus leading to permeability damage.

In the DBF model a horizontal flow is considered, where gravity is neglected. Both asphaltene precipitation and deposition are described by mass balance models for the liquid and the solid (= asphaltene) phase, the momentum balance and porosity and permeability reduction models (Civan 2001; Wang and Civan 2001; Wang and Civan 2005). The mass balance equation for the oil in the liquid phase is given in:

$$\frac{\partial}{\partial t}(\phi \rho_L w_{OL}) + \frac{\partial}{\partial x}(\rho_L u_L w_{OL}) = 0 \quad (2.36)$$

where, O = oil component, i.e. maltenes; L = liquid component; ϕ = porosity; ρ_L = density of the liquid phase; u_L = velocity of the liquid phase; w_{OL} = mass fraction of the oil in the liquid phase

The mass balance for asphaltenes is given by:

$$\frac{\partial}{\partial t}(\phi C_A \rho_A + \phi \rho_L w_{AL}) + \frac{\partial}{\partial x}(\rho_L u_L w_{SAL} + \rho_L u_L w_{AL}) = -\rho_A \frac{\partial E_A}{\partial t} \quad (2.37)$$

where, A = asphaltenes; C_A = volume fraction of suspended asphaltenes precipitating in the liquid phase; ρ_A = asphaltene density; w_{SAL} = mass fraction of suspended asphaltenes, which can precipitate; w_{AL} = dissolved asphaltenes in the liquid phase; E_A = volume fraction of deposited asphaltenes

Darcy's law for porous media can be used to describe the momentum balance:

$$u_L = \frac{k}{\mu_L} \frac{\partial p}{\partial x} \quad (2.38)$$

where, k = absolute permeability of the porous medium; μ_L = viscosity of the liquid; $\partial p/\partial x$ = pressure drop across the porous medium

2.5.2.1 Deposition Model

Asphaltene damage to the reservoir rock can occur due to surface deposition, entrainment and pore throat plugging. As asphaltene deposits accumulate on the pore surface, the pore space for the oil phase becomes smaller. As the flow passages are narrowed down, the increasing shear rate may overcome a critical value and some deposits are swept away and entrained by the liquid phase. When asphaltene deposits accumulate in front of a pore, they can plug them (Figure 2.7).

The net deposition rate is then given in:

$$\frac{\partial E_A}{\partial t} = \underbrace{\alpha C_A \phi}_{\text{Surface Deposition}} - \underbrace{\beta E_A (v_L - v_{L,cr})}_{\text{Entrainment}} + \underbrace{\gamma u_L C_A}_{\text{Plugging}} \quad (2.39)$$

where, E_A = volume fraction of deposited asphaltenes; v_L = interstitial velocity ($= u_L/\phi$); $v_{L,cr}$ = critical interstitial velocity; u_L = superficial velocity; α = surface deposition coefficient; β = entrainment rate coefficient; γ = pore throat plugging coefficient

According to Wang (2000) and Boek et al. (2011), the surface deposition rate (first term of Equation (2.39)) based on the pore volume is proportional to the concentration of particles suspended in the flowing fluid. The surface deposition rate based on the bulk volume is related to the concentration of suspended asphaltene precipitates and the pore volume occupied by the liquid. The second term describes the entrainment of particles by the liquid phase. Entrainment becomes dominant once

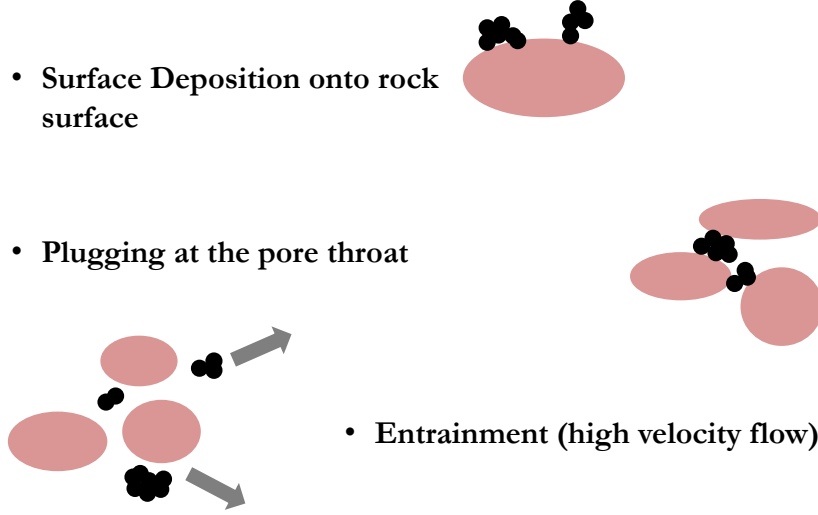


Figure 2.7: Mechanisms for asphaltene damage in a reservoir rock.

the interstitial velocity exceeds the critical interstitial velocity. Furthermore, Equation (2.39) describes, that entrainment is proportional to the amount of deposits. The last term describes the plugging contribution to the net deposition, where the plugging rate is proportional to the superficial velocity and the asphaltene precipitates in the suspension. The value of the entrainment coefficient β is set as β_i , when $v_L > v_{L,cr}$ and otherwise to zero. Wang (2000) defined the value of γ as:

$$\begin{aligned} \gamma &= \gamma_i(1 + \sigma E_A), \text{ if } D_{pt} \leq D_{pt,cr} \\ \gamma &= 0, \text{ otherwise} \end{aligned} \quad (2.40)$$

where, σ = deposition constant (saying that the pore throat plugging deposition rate increases with total deposits); D_{pt} = average pore throat diameter; $D_{pt,cr}$ = critical pore throat diameter (constant)

Equation (2.40) states that when the average pore throat diameter is smaller than the critical one, pore throat plugging will occur.

2.5.2.2 Porosity and Permeability Reduction Models

Asphaltene deposition in a rock reservoir may lead to a decrease in the porosity ϕ and the permeability k . Wang and Civan (2001) proposed that the instantaneous, local porosity due to deposition can be calculated from the difference between the initial porosity (ϕ_0) and the fraction of asphaltene deposits (E_A).

$$\phi = \phi_0 - E_A \quad (2.41)$$

The change in permeability as a function of porosity is given by (Civan et al. 1989; Wang 2000):

$$k = k_0 \left(\frac{\phi}{\phi_0} \right)^3 \quad (2.42)$$

Lawal et al. (2011) stated that the exponent in the power law relationship can nearly always be treated as an adjustable parameter. The exponent is dependent on intrinsic flow parameter and for most rocks it falls within the range of 2 - 10. Reis and Acock (1994) recommended that the best value for a sandstone would be 5. Ring et al. (1994) compared the suggested value from Civan and Knapp (1987) for the permeability reduction model (exponent = 3 for sand particles) to their own work for paraffin particles and obtained a good fit for the power law expression when an exponent of 8 was chosen.

The DBF model by Wang and Civan (2001) and Wang and Civan (2005) was later extended by Kord et al. (2014) accounting for a fourth mechanism to describe

asphaltene damage, known as pore throat opening. This process occurs when previously plugged pore throats are opened up again as a result of the high fluid velocity, leading again to an increase in the permeability. The model by Kord et al. (2014) suggests therefore that there is a counterbalance between permeability reduction (due to adsorption) and restoration (due to entrainment). Eventually a steady state will be reached where the rate of surface deposition is equal to the rate of entrainment. Beyond the steady state, pore throat plugging may occur, resulting eventually in pore throat opening.

2.5.3 Stochastic Rotation Dynamics (SRD)

SRD is mesoscopic simulation technique for the hydrodynamics of complex fluids which may be a challenge for conventional techniques such as Molecular Dynamics (MD) or Monte Carlo (MC) due to the length of timescale. SRD is a useful method to study hydrodynamics of colloidal particles, such as asphaltenes. In this method, the fluid is modelled by a large number of N particles ($\approx 10^5$), where particle positions and velocities are continuous variables. The particles move in a continuous space and discretely in time (Kikuchi et al. 2003). In general, it consists of two steps: *(i)* a free streaming step and *(ii)* a collision step. In the beginning of the simulation the particles are distributed in the simulation box. In the streaming step, the particle positions $r_i(t)$ are updated according to the following equation:

$$r_i(t + \delta t) = r_i(t) + v_i(t)\delta t \quad (2.43)$$

where, r_i = position of the particle; $v_i(t)$ = particle velocity; δt = discrete time step of the evolution of the system.

In this step, the particles perform a uniform, linear motion without interactions among them. The interaction between the particles are considered in the second

step of the algorithm: The collision step, while conserving the total momentum and energy of each cell. The collisions are modelled using stochastic rotation of the relative velocity of each particle in the cell. In the collision step, the particle velocity is updated, where the centre of mass velocity v_{cm} is calculated using the following expression:

$$v_{\text{cm}} = \frac{1}{N} \sum_{i=1}^N v_i \quad (2.44)$$

where, N = number of particles in the cell

Subsequently, the particle velocities are transformed in each cell.

$$v_i(t + \delta t) = v_{\text{cm}}(t) + R(v_i(t) - v_{\text{cm}}(t)) \quad (2.45)$$

where, R = Rotation matrix defined for each cell, which performs a rotation of a different certain angle in each cell.

Using the SRD algorithm, fluids motion can be simulated which are described by the Navier-Stokes equation. The fluid and its properties can be described using several parameters such as the mean free path, size of one cell, density, thermal energy and rotation angle (Ihle and Kroll 2001; Boek et al. 2008; Boek et al. 2010).

2.5.4 Lattice-Boltzmann (LB)

Lattice-Boltzmann (LB) can be seen as the kinetic approach to computational fluid dynamics (CFD). Nowadays, LB is used in many industries and engineering fields dealing with transport phenomena due to its efficiency and accuracy.

LB modelling is performed by considering virtual particles moving along a discrete lattice. The particles interact according to collision rules which comprise mass and momentum conservation. LB equations are used to describe the time develop-

ment of the particle distribution function (Ihle and Kroll 2001).

Lattice Boltzmann Equation According to Sukop and Thorne (2006) the idea behind LB is the Boltzmann gas concept. Using kinetic theory and statistical dynamics, a simplified version of the Boltzmann equation can be derived. The probability of finding a molecule with a specific position x and momentum p at a given time t is described by the *single particle distribution function* $f^{(1)}(x^N, p^N, t)$. Similar to SRD, two steps (streaming and collision) can be defined. The streaming process can be described with Equation (2.46).

$$f^{(1)}(x + dx, p + dp, t + dt)dx dp = f^{(1)}(x, p, t)dx dp \quad (2.46)$$

Due to collisions between the particles, Sukop and Thorne (2006) included in Equation (2.46), the term $\Gamma^{(-)}dx dp dt$ and $\Gamma^{(+)}dx dp dt$ to account for the collision effect. Adding these expressions to $f^{(1)}$ leads to Equation (2.47).

$$f^{(1)}(x + dx, p + dp, t + dt)dx dp = f^{(1)}(x, p, t)dx dp + [\Gamma^{(+)} - \Gamma^{(-)}]dx dp dt \quad (2.47)$$

Finally, the first order terms of a Taylor series expansions results in the Boltzmann (Equation (2.48)).

$$v \cdot \nabla_x f^{(1)} + F \cdot \nabla_p f^{(1)} + \frac{\partial f^{(1)}}{\partial t} = \Gamma^{(+)} - \Gamma^{(-)} \quad (2.48)$$

The lattice-Boltzmann models were designed to simplify the original concept of the

Boltzmann gas concepts. The numbers of particles spatial positions and momenta were reduced from continuum to a smaller, discrete number of steps. Particle positions are defined as the nodes of a lattice and the variation in momenta were reduced to 8 directions, 3 magnitudes and a single mass. Several choices regarding the lattice for LB can be made. Usually, the $D\alpha Q\beta$ - Notation is used to describe a lattice, where α and β indicate the dimensionality of the applied lattice and the number of discrete velocities, respectively. Figure 2.8 shows an example for a D2Q9 lattice type. The shown model is 2-dimensional and contains 9 velocities.

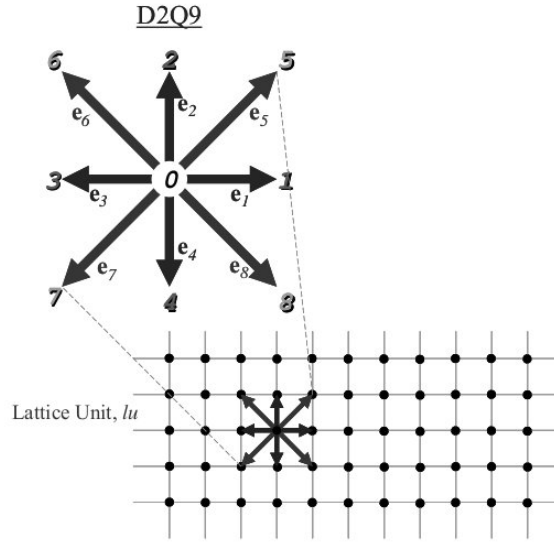


Figure 2.8: The D2Q9 Model Lattice (Sukop and Thorne 2006).

e_a = velocity; a = direction index $(0, 1, \dots, 8)$; e_0 = particles at rest; lu = lattice unit.

Similar to the continuous function in Equation (2.47), a single particle distribution function f can be included which defines a frequency of occurrence. Accordingly, the macroscopic fluid density is defined as follows:

$$\rho = \sum_{i=0}^8 f_a \quad (2.49)$$

The average of the microscopic velocities e_a is the macroscopic velocity u :

$$u = \frac{1}{\rho} \sum_{i=0}^8 f_a e_a \quad (2.50)$$

The expression in Equation (2.50) allows to determine the macroscopic velocities, representing the fluid's motion, from the discrete microscopic velocities. Subsequently, several approaches can be used to describe the streaming and collision of the particles via the distribution function. An example for such an approach is the Bhatnagar-Gross-Krook (BGK) approximation. In the BGL approach, both the streaming and collision steps are defined as follows:

$$\underbrace{f_a(x + e_a \Delta t, t + \Delta t) = f_a(x, t)}_{\text{Streaming}} - \underbrace{\frac{[f_a(x, t) - f_a^{eq}(x, t)]}{\tau}}_{\text{Collision}} \quad (2.51)$$

Although they are defined as a single expression in Equation (2.51), both streaming and collision step must be separated if solid boundaries are present ($\rightarrow$ since bounce back boundary condition is defined as a separate collision). Therefore, the equilibrium distribution function f^{eq} for the D2Q9 model lattice can be derived:

$$f_a^{eq}(x) = w_a \rho(x) \left[1 + 3 \frac{e_a \cdot u}{c^2} + \frac{9(e_a \cdot u)^2}{2c^4} - \frac{3u^2}{2c^2} \right] \quad (2.52)$$

where, w_a = weights which are 4/9 for the particles at rest $a = 0$, 1/9 for $a = 1, 2, 3, 4$ and 1/36 for $a = 5, 6, 7, 8$; c = basic speed on the lattice: $1 \text{ lu} \cdot \text{ts}^{-1}$ in the simplest implementation.

Before obtaining results, it is necessary to define boundary conditions, such as periodic, bounceback, constant pressure and constant velocities (Sukop and Thorne 2006). The LB method has several applications, such as modelling the hydrodynamic

interactions of fluid flow in porous media. Fundamental questions of single-phase and multi-phase flow might be answered and determined, such as the microscopic basis of the macroscopic transport or the size dependency of the macroscopic transport properties (Ferreol and Rothman 1995). This can be achieved by calculations to determine the variation of the permeability within a rock sample and by numerical investigations of the pore-scale porous media flow.

2.5.5 Comparison between LB and SRD

Yeomans (2006) compared the two mesoscale simulations methods and described their application to investigate the physics of complex fluids. LB does not include fluctuations and is defined as an unusual finite difference solution of the Navier-Stokes equation, whereas the SRD method is a simple approach for the mesoscale modelling methods. SRD solves the equations of fluctuating hydrodynamics, taking into account Brownian motion. According to Yeomans (2006), SRD can be defined as a heat bath transporting momentum. Hegde et al. (2011) used the SRD and LB simulation techniques to compare

the diffusion coefficient and chain length of polymers in solution (Figure 2.9). Good agreement was found regarding the gyration radius and diffusivity, using the different simulation approaches. The top image shows the SRD simulation with point-like solvent particles in a simulation box and the bottom one the LB simulation with points on the lattice. The velocities are represented by arrows.

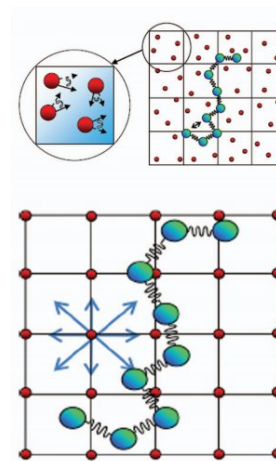


Figure 2.9: Schematic of the simulated interaction of a polymer chain in a solvent (Hegde et al. 2011).

Chapter 3

Asphaltene Precipitation with Hydrocarbons and CO₂

3.1 Introduction

Carbon dioxide (CO₂) flooding during enhanced oil recovery (EOR) operations may trigger the precipitation and deposition of asphaltenes (Leontaritis and Mansoori 1988; Jafari Behbahani et al. 2012). Further research is required on identifying the conditions that will initiate precipitation. The following work aims to improve the understanding of the effect of changing precipitant fraction in a crude oil+precipitant mixture on asphaltene precipitation. The systems compared in this work are a crude oil+hydrocarbon and a crude oil+CO₂ mixture.

Asphaltene precipitation by filtration experiments is an efficient and suitable way to determine the onset point and the amount of asphaltenes precipitated as a function of precipitant volume. This method has been well established for liquid hydrocarbon precipitants (Buenrostro-Gonzalez et al. 2004), but little information is available from experiments with CO₂. The CO₂ induced precipitation experiments are carried out in a high pressure-high temperature (HPHT) filtration cell, filled

with a known amount of crude oil and pressurised with CO₂.

The onset point is quantified in terms of the Hildebrand solubility parameter, where the applicability to asphaltene precipitation with hydrocarbons has been well established by Buckley et al. (1998) and Buckley and Wang (2002). This theory is used here to reconcile the behaviour of different hydrocarbon precipitants and compare it to the crude oil+CO₂ system.

Due to the complexity of the crude oil+precipitant mixture leading to asphaltene precipitation, a simplified picture is presented at the end of this chapter from a thermodynamic perspective by calculating a p - T diagram of a model crude oil. Asphaltene precipitation is defined in this analysis as a liquid-liquid phase separation, treating the asphaltene as a pseudoliquid.

3.2 Materials and Methodology

3.2.1 Crude Oil

For all experiments presented in the following chapters, a heavy crude oil from Zuata, Venezuela was used, which was provided by Shell Global Solution, The Netherlands. Selected properties of the crude oil are presented in Table 3.1.

Table 3.1: Zuata crude oil properties.

Characteristics	Value
API Gravity ^a	9.28
C7-asphaltene content ^b	16.1wt%
Kinematic viscosity ($T = 298$ K) ^a	295 Pa·s
Kinematic viscosity ($T = 323$ K) ^b	5.4 Pa·s
Molar mass ^b	approx. 529 g/mol
Refractive index n ($T = 293$ K) ^b	1.5695
Hildebrand solubility parameter ^b	19.96 MPa ^{0.5}

^adata provided by Shell Global Solutions International B.V., Amsterdam, The Netherlands

^bdata measured in this laboratory

3.2.2 Refractive Index Measurements

To calculate the solubility parameter for a component i , Buckley et al. (1998), Buckley and Wang (2002), and Wang and Buckley (2003) established a relationship between the solubility parameter and the refractive index n of a component:

$$\delta_i = 52.042 \times F_n + 2.904 \quad (3.1)$$

Where F_n is defined as:

$$F_n = \frac{n^2 - 1}{n^2 + 2} \quad (3.2)$$

The refractive indices for the crude oil, solvents and precipitants were measured at $T = 298$ K with an automatic refractometer (Index Instruments GPR 12-70E), which uses the Sodium-D-line ($\lambda = 589$ nm) as the wavelength. The critical angle technique allows for determining the refractive index of an opaque liquid like crude oil. Volatile solvents such as toluene may evaporate partially during the measurement, therefore the measurements were carried out within a very short period of time and the refractometer was sealed to minimise evaporation. To obtain a reliable mean value,

three repeat measurements were taken for each component. The accuracy of the refractometer is ± 0.0001 refractive index units.

The refractive indices and δ_i for crude oil and the set of hydrocarbons used in the filtration experiments are shown in Table A.1 - Table A.5. Very good agreement was found between the measured values here and the ones reported in the literature (Blanks and Prausnitz 1964; Chao and Seader 1961).

3.2.3 Asphaltene Precipitation with Hydrocarbons

For the filtration experiments, 0.983 g of crude oil (corresponds to 1 mL) were mixed with 40 mL of a toluene+hydrocarbon mixture at different ratios. The crude oil+solvent+precipitant mixture was stirred for 30 seconds using a magnetic stirrer and then stored in sealed glass bottles at ambient and dark conditions for 48 hours. This procedure allows the system to reach thermodynamic equilibrium, avoid evaporation of solvents and light crude oil components and possible asphaltene oxidation. Repeat experiments at various time scales were carried out to ensure that 48 hours were adequate to equilibrate the mixture. The sample was then filtered through a hydrophilic filter paper (OFITE, $2.7 \mu\text{m}$) using a vacuum pump (D-Lab Diaphragm Pump, Edwards) to recover the precipitated asphaltenes. The time taken during this step lied in between 30 seconds (for mixtures with no asphaltenes) and a maximum of two minutes (for the mixture with the highest asphaltene yield). To wash out remaining maltenes or other crude oil fractions, the asphaltenes were washed using a mixture of solvent+precipitant in the same ratio until the filtrate was colourless. After completed filtration, the filter paper and precipitated asphaltenes were dried in an oven ($T = 348 \text{ K}$) for 25 minutes. This time was found to be sufficient to obtain steady weight. The mixture solubility parameter δ_{mixture} was calculated using

the volume fraction φ of each component i in the mixture.

$$\delta_{\text{mixture}} = \sum_i \varphi_i \delta_i \quad (3.3)$$

The mixture compositions, the mass of the filter papers before and after vacuum filtration and the calculated δ_{mixture} are shown for three different precipitants in Table A.7, Table A.8 and Table A.9. Two repeat runs were carried out with heptane as a precipitant, the averaged values are reported in Table A.7.

3.2.3.1 Filtration at $T = 323$ K

To investigate the effect of temperature on asphaltene precipitation, the filtration experiments were also carried out at a temperature of $T = 323$ K. The experimental filtration procedure remained as described previously. To heat up the sample to the desired temperature and ensure isothermal conditions, the crude oil+diluent mixture was stored in a water bath which was kept at constant temperature. The filtration set-up remained at ambient conditions, but the effect of this discrepancy was limited by the short time taken in this step (approximately 15 seconds to 2 minutes).

The mixture compositions for the crude oil+toluene/heptane (heptol) mixture and the mass of the filter papers before and after vacuum filtration are shown in Table A.10. Heptane was the only precipitant investigated at $T = 323$ K.

3.2.4 Asphaltene Precipitation with CO₂

The high pressure-high temperature (HPHT) experiments with CO₂ were carried out in a filtration cell (OFITE #171-84-01) at $T = 323$ K and within a pressure range from 30 - 240 bar. The set-up is shown in Figure 3.1.

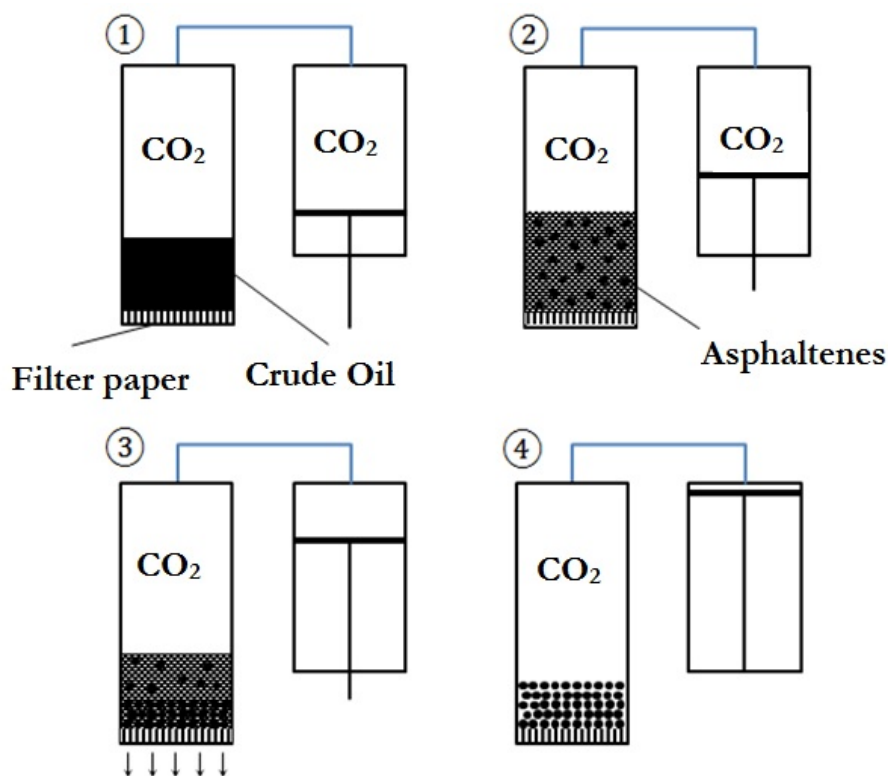


Figure 3.1: HPHT filtration set-up for asphaltene precipitation with CO₂.

Two different samples were studied: The original crude oil and, due to its high viscosity, a diluted version. The crude oil was diluted with toluene to obtain a mixture of 70wt% crude oil+30wt% toluene. A filter paper (OFITE, 2.7 μm) was placed in the pressure cell which was then filled with approximately 12 g of the diluted crude oil or 1-2 g of the original one. In the case of the undiluted crude oil, less has been used due to the increased difficulty associated with loading it into the cell. The mixture was pressurised with CO₂ using a syringe pump (ISCO #500-D, U.S.) (Figure 3.1-1). The cell was kept at constant pressure and temperature for 48 hours (further discussion regarding the time span follows below) which allows asphaltenes to form a separate solid phase (Figure 3.1-2). The oil and CO₂ were then released through the bottom of the cell (Figure 3.1-3) with the asphaltenes

remaining on the filter paper (Figure 3.1-4), which was then dried in an oven at $T = 423$ K for 48 h. For comparative purposes the experiments were repeated, where the diluted crude oil was pressurised with Helium.

Table A.12, Table A.13 and Table A.14 summarise the experimental conditions, showing the mass of crude oil in the pressure cell, the mass of filter paper before and after the experiment and indicates how much residual oil was subtracted to obtain the wt% of precipitated asphaltenes.

To describe the asphaltene precipitation in term of the solubility parameter, the approach by Allada (1984) was applied to calculate the solubility parameter of CO₂:

$$\delta_r = \left[\frac{C_1}{R} \frac{(E^* - E)}{T_c} \frac{p_r}{T_r} \frac{1}{Z} \right]^{0.5} \quad (3.4)$$

$$\therefore \delta = \left[\frac{10^3 \times p_c (E^* - E) \left(\frac{p}{p_c} \right)}{RT_c Z \left(\frac{T}{T_c} \right)} \right]^{0.5} \quad (3.5)$$

where, δ_r = reduced solubility parameter ($\delta/(p_c^{0.5})$); T_r = reduced temperature (T/T_c); p_r = reduced pressure (p/p_c); E = internal energy; E^* = internal energy isothermally expanded to “zero” pressure; Z = compressibility factor; C_1 = conversion factor ($\text{cal}/\text{cm}^3 \times \text{atm}$)

3.2.4.1 Thermodynamic Equilibrium at HPHT

To ensure full thermodynamic equilibrium while at the same time allowing for asphaltene precipitation, the mixture remained in the pressure cell for different time spans (1-4 days) at constant pressure ($p = 180$ bar) and temperature ($T = 323$ K) to then determine the amount of precipitated asphaltenes. Two consecutive runs were carried out. By comparing the averaged results including their standard devi-

ation in Figure 3.2, it was concluded that two days were sufficient to ensure system equilibrium.

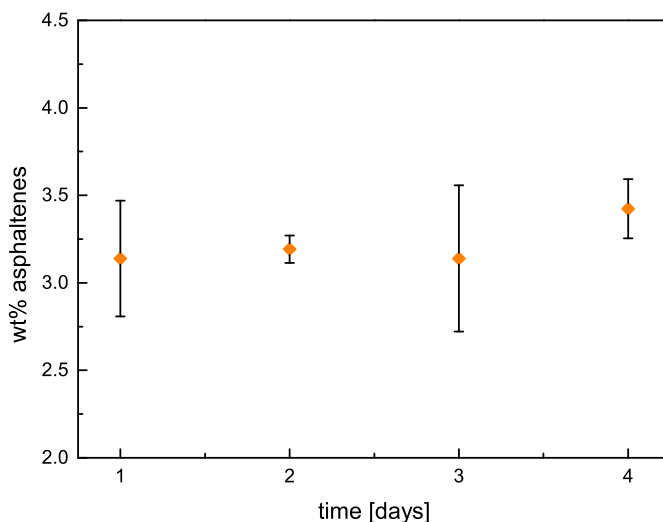


Figure 3.2: Average amount of precipitated asphaltene at a constant pressure ($p = 180$ bar) and temperature ($T = 323$ K) at different equilibria times for two repetitions.

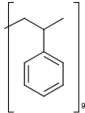
3.2.5 Phase Behaviour Modelling

The following section describes the computational method used to predict the phase behaviour of a crude oil model with the implementation of the UNIFAC-FV model using Aspen Polymers. This software is a widely used process modelling tool for polymer simulation processes, while at the same time being user-oriented and commercially supported, thus being the ideal tool for the present work. For the crude oil model studied, Aspen performed flash calculations at each pressure and temperature on a p - T -grid, which established the number of phases and the composition at each point on the grid. This approach is applicable to calculations of vapour-liquid equilibrium (VLE), liquid-liquid equilibrium (LLE) and vapour-liquid-liquid equilibrium

(VLLE).

The Crude Oil Model To represent the Zuata crude oil, a model based on the estimated molar mass of the crude oil, while at the same time being a stable system at ambient conditions, was developed based on previous work by Guilbaud et al. (2015). The model has four components; with eicosane (C20) and dodecane (*n*-C12) representing the alkanes, cumene depicts the aromatic component and polystyrene with nine repeat units, PS9, represents the asphaltenic part of the crude oil. Heptane (C7) acts as a precipitant to induce instabilities in the phase behaviour.

Table 3.2: The crude oil model.

Component	Group	Multiplicity	Representation	Mole fraction x
Eicosane	CH ₃	2		0.335
	CH ₂	18		
Cumene	CH ₃	2		0.321
	aCCH	1		
	aCH	5		
Dodecane	CH ₃	2		0.343
	CH ₂	10		
PS9	CH ₃	2		0.001
	CH ₂	9		
	aCCH	9		
	aCH	45		
Heptane	CH ₃	2		/
	CH ₂	5		

Specifying the PS9 Component in Aspen Polymers The styrene segment (in Aspen defined as: STY-SEG) was used to define the structure of PS9 as an oligomer. This method was chosen because oligomers have a defined number of repeat segments whereas polymers are mostly defined through their polydispersity. The thermophysical properties of an oligomer lie between those of the polymer and

the monomer. The values for the pure components were taken from AspenTechnology (2011).

Property Models and Methods in Aspen Polymers The Polymer UNIFAC-FV model is part of the Activity Coefficient Models and extends the UNIFAC model by taking into account free volume effects which is important for polymers. Similar to other group contribution methods it is a purely predictive model. Applying the model to VLE calculations requires another model for the vapour phase, usually an equation of state (EoS). The different methods and models used to calculate thermodynamic properties are part of property methods in Aspen Polymers. The built-in property method used here is called POLYUFV and uses the Soave-Redlich-Kwong (SRK) EoS to calculate the vapour phase properties. SRK is the primary choice of property model as it yields accurate equilibrium calculations for systems from low to high temperature regions and further has the ability to predict VLE using parameters derived from low-pressure data by employing the UNIFAC parameter matrix.

UNIFAC-FV Parameters The components structure is divided into groups and sub-groups. The contributions for each group were taken from Danner and High (1993). Table 3.3 summarises the type and quantity of sub-groups used in the calculations, the group volume parameter R_k and the group area parameter Q_k . The interaction parameters b_{mk} among each sub-group are given in Table 3.4.

Table 3.3: UNIFAC sub-groups and their parameters.

Sub-group	ASPEN group number	R_k	Q_k
CH ₃	1015	0.9011	0.848
CH ₂	1010	0.6744	0.640
aCCH	1150	0.5313	0.400
aCH	1105	0.8121	0.348

Table 3.4: UNIFAC interaction parameters for the sub-groups. CH₂ and CH₃ belong to the same main-group “CH₂”, hence their interaction was set to zero.

b_{mk}	aCCH	aCH	CH₂	CH₃
aCCH	0	-146.8	-69.7	-69.7
aCH	167	0	-11.12	-11.12
CH₂	76.5	61.13	0	0
CH₃	76.5	61.13	0	0

SRK Parameters The pure components parameter required in the vapour phase model are given in Table 3.5. The built-in binary interaction parameter k_{ij} , which are used automatically in the SRK property method, are displayed in Table 3.6.

Table 3.5: SRK pure components parameters.

Component	T_c [K]	p_c [MPa]	Acentric factor ω
Eicosane	768	1.2	0.907
Cumene	631	3.2	0.327
Dodecane	658	1.8	0.576
PS9	500	2.0	0.296
Heptane	540	2.7	0.349

Table 3.6: SRK binary interaction parameters. Please note, $k_{ij} = k_{ji}$

i	PS9	PS9	PS9	PS9	C20	C20	C20
j	C20	Cumene	<i>n</i>-C12	C7	Cumene	<i>n</i>-C12	C7
k_{ij}	-0.309	-0.260	-0.284	-0.294	0.001	-0.005	-0.024

i	Cumene	Cumene	<i>n</i>-C12
j	<i>n</i>-C12	C7	C7
k_{ij}	0.021	0.029	-0.007

3.3 Results and Discussion

Firstly, in Section 3.3.1 the filtration results are analysed for three different hydrocarbon precipitants at ambient conditions in terms of the amount of precipitant and δ_{mixture} . The results for heptane are then compared to heptane induced precipitation at $T = 323$ K in Section 3.3.2. Subsequently, the effect of CO_2 on precipitation with changing pressure is shown in Section 3.3.3. As the assumption of full miscibility is no longer valid in the case of a crude oil+ CO_2 mixture, solubility measurements (Hu et al. 2016; Hu 2016) are depicted in Section 3.3.4. Thereafter the concept of the solubility parameter is applied once more with the aim to describe precipitation in a more predictive way (Section 3.3.5). Finally, Section 3.3.6 concludes with a brief insight into the thermodynamic perspective, where precipitation in the four component crude oil model is qualitatively analysed.

3.3.1 Filtration Experiments at Ambient Conditions

Three precipitants and their effect on asphaltene precipitation are compared in Figure 3.3, where the wt% of precipitated asphaltenes is plotted versus the amount of toluene in the mixture. At a high toluene fraction, no asphaltenes precipitated from the crude oil+diluent mixture. By changing the diluent ratio towards more hydrocarbon precipitant, the precipitation onset point was identified within the range of 45-50vol% toluene, with C7-asphaltenes requiring the most volume of hydrocarbon to precipitate. Beyond the onset point, the mass of precipitated asphaltenes increases linearly with volume of precipitant.

By plotting the mixture solubility parameter δ_{mixture} instead of the toluene volume fraction (Figure 3.4), the same precipitation onset point is observed. By extrapolating the yields, the precipitation onset point for the Zuata crude oil was calculated as $\delta_{\text{mixture}} = (16.45 \pm 0.13) \text{ MPa}^{0.5}$. Both the solubility parameter at

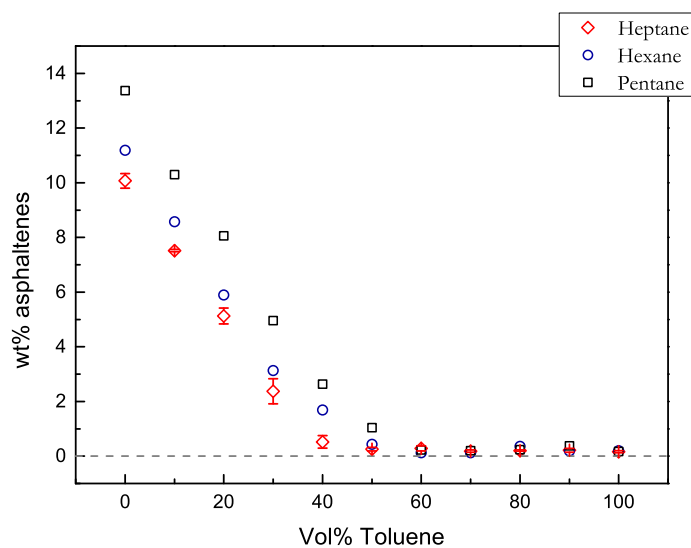


Figure 3.3: Asphaltenes precipitated with different light hydrocarbons (*n*-heptane, *n*-hexane and *n*-pentane) as a function of volume% of toluene in the crude oil+solvent+precipitant mixture.

the onset point and the slope can be used to estimate the amount of asphaltenes precipitated for any given liquid hydrocarbon.

Differences, however, can be observed in the maximum amount of asphaltenes precipitated with different hydrocarbons: At a given solvent-to-precipitant ratio, *n*-pentane (C5) precipitates more asphaltenes than *n*-hexane (C6) and *n*-heptane (C7) (Figure 3.5). This indicates that precipitants with a shorter carbon-length act as a stronger asphaltene precipitant within the experimental conditions investigated.

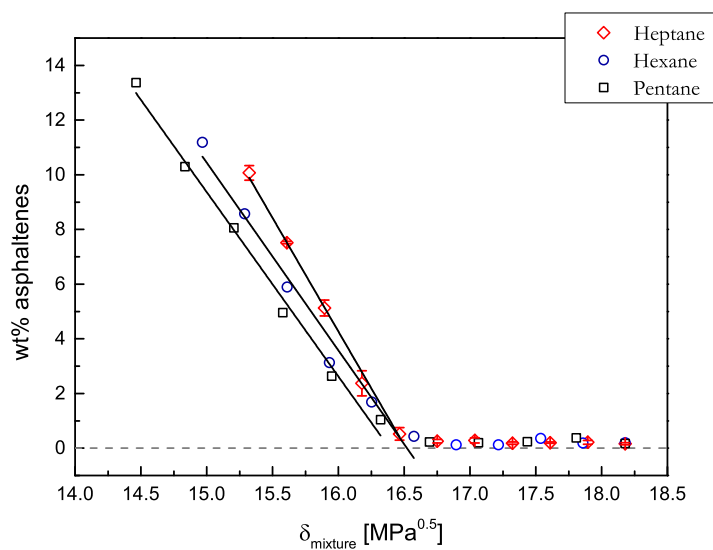


Figure 3.4: Asphaltenes precipitated with different light hydrocarbons (*n*-heptane, *n*-hexane and *n*-pentane) at different mixture solubility parameter δ_{mixture} .

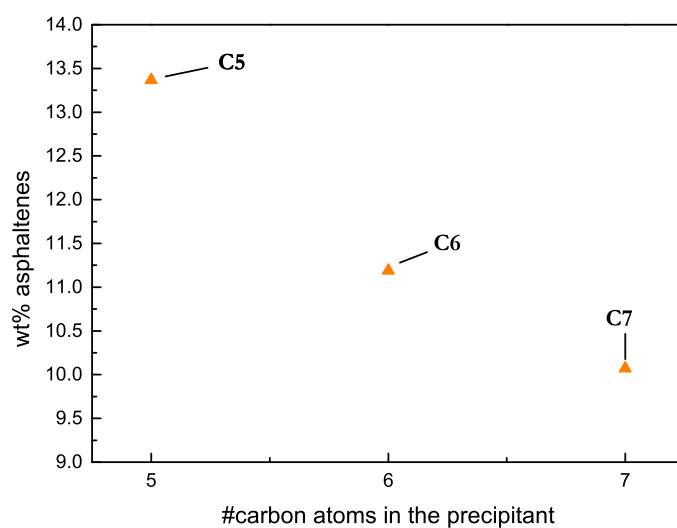


Figure 3.5: Maximum amount of precipitated asphaltenes induced by C5-C7.

3.3.2 Filtration Experiments at $T = 323$ K

According to Maqbool et al. (2011), an increase in temperature seems to favour asphaltene stabilisation in crude oil. To investigate the effect of temperature on precipitation in the Zuata crude oil, the previous experiments were repeated at elevated temperature. Figure 3.6 compares the heptane induced precipitation behaviour at $T = 298$ K and $T = 323$ K as a function of changing vol% of solvent in the crude oil+heptol mixture.

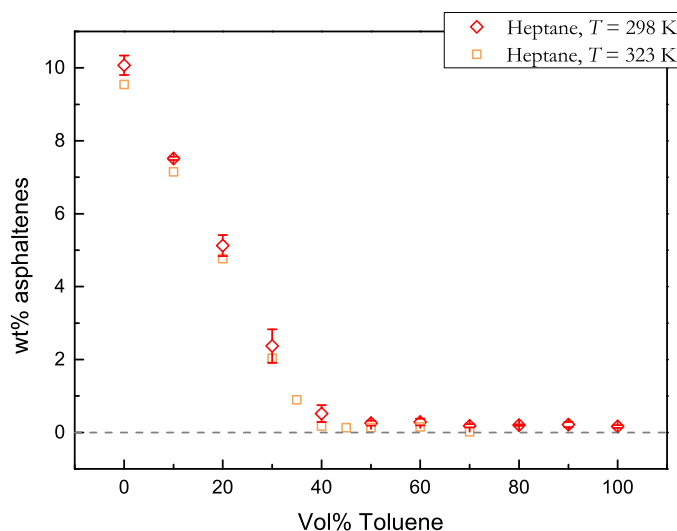


Figure 3.6: Asphaltene precipitation at different temperatures as a function of vol% of solvent. The asphaltenes were precipitated with *n*-heptane from a crude oil+heptol mixture at two different temperatures: $T = 298$ K and $T = 323$ K.

Both sets respond equally to the change in heptane to toluene ratio: No asphaltenes precipitated at a high solvent fraction and the wt% of precipitated asphaltenes increases linearly with increasing precipitant fraction beyond the onset point. Temperature does not seem to have a significant effect on either the precipitation onset point or the initial asphaltene yields beyond the onset. However, less asphaltenes precipitated in the pure heptane environment at $T = 323$ K, indicating

higher solubility of the asphaltenes in crude oil at higher temperature and therefore a higher oil stability with respect to asphaltene precipitation.

Two different approaches to calculate the mixture solubility parameter at elevated temperature were investigated as shown below.

Approach 1: Applying the Linear Relationship for Non-Polar Liquids by Measuring the Refractive Index at $T = 323\text{ K}$ The correlation described in Equation (3.1) was used to calculate δ_i for ambient conditions. Considering the dependence on F_n and hence the refractive index, the same approach was applied to establish a new linear relationship at $T = 323\text{ K}$: The refractive indices of different alkanes were measured at $T = 323\text{ K}$ (Table A.6). The solubility parameters for these alkanes were calculated with a relationship established by Vargas and Chapman (2010).

$$\delta^2(p, T) = \delta_0^2(p, T_0) \exp[-\alpha_p(T - T_0)] \quad (3.6)$$

where, T_0 = reference temperature; α_p = thermal expansion coefficient

The new correlation was then calculated via linear regression using the measured refractive indices:

$$\delta_i = 51.714 \times F_n + 2.7832 \quad (3.7)$$

The linear relationship from Equation (3.7) is visualized in Figure 3.7. By applying Equation (3.7), δ_i for any liquid hydrocarbon at $T = 323\text{ K}$ can be calculated.

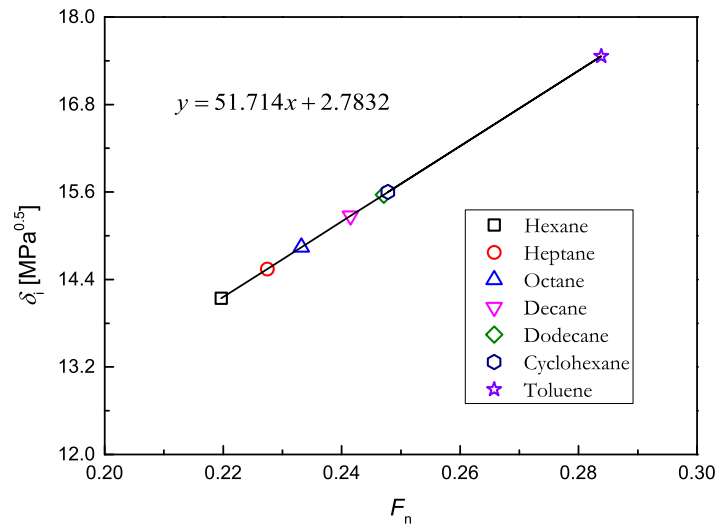


Figure 3.7: Calculated F_n from measured refractive indices for various hydrocarbons at $T = 323$ K.

Approach 2: The Change of Heat of Vaporisation ΔH with Temperature According to Hildebrand and Scott (1964), the Hildebrand solubility parameter is defined as the square-root of the cohesive energy density:

$$\delta = \sqrt{\frac{\Delta H - RT}{V_m}} \quad (3.8)$$

where, ΔH = heat of vaporisation; V_m = molar volume

The cohesive energy density is equal to the ratio of the heat of vaporisation of a compound and its molar volume in the condensed phase. The enthalpy of vaporisation ΔH is described as the change in enthalpy required to transform a liquid into its gaseous form at constant pressure. The heat of vaporisation is temperature dependent and decreases with increasing temperature until it vanishes completely at the critical temperature T_c of a component. The change of ΔH for toluene (Table A.11) and heptane (Table A.11) was evaluated with data obtained from the National In-

stitute of Standards and Technology database (NIST) (Linstrom and Mallard 2010) with a relationship established by Majer et al. (1985):

$$\Delta H = A \times \exp(-\beta T_r)(1 - T_r)^\beta \quad (3.9)$$

where, A and β = empirical coefficients

The decrease of ΔH with temperature for both toluene and heptane is graphically represented in Figure 3.8.

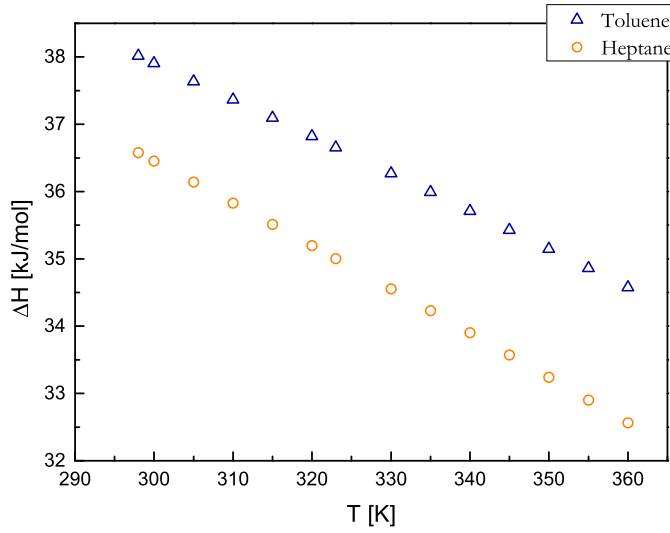


Figure 3.8: Decreasing heat of vaporisation ΔH with increasing temperature for the pure components toluene and heptane.

The molar volume V_m for each component was calculated using the molar mass and the density at a given temperature. The density with changing temperature was taken from NIST.

$$V_m = \frac{M}{\rho} \quad (3.10)$$

where, M = molar mass

By inserting the values for V_m and ΔH into Equation (3.8), the solubility parameters δ_{toluene} and δ_{heptane} were calculated.

Table 3.7 summarises the solubility parameters obtained through the two approaches described above, which are then compared to the experiments at $T = 298$ K in terms of δ_{mixture} in Figure 3.9.

Table 3.7: The solubility parameters at $T = 323$ K estimated by the two different approaches.

δ_i	Approach 1	Approach 2
Toluene	17.48	17.59
Heptane	14.55	14.57
Crude oil	19.07	19.49 ^a

^acalculated from density change and estimated M at $T = 323$ K.

Both data sets show a shift towards lower mixture solubility parameter, which is due to the change of δ_i for crude oil, toluene and heptane, suggesting that the concept of the solubility parameter may not be suitable to provide a prediction of asphaltene precipitation from crude oil at different temperatures. Furthermore, the solubility parameter of the asphaltenes may change at higher temperature, which will influence the crude oil's precipitation behaviour. Diallo et al. (2000) simulated the effect of temperature on δ_a in a range from 200 to 500 K from an asphaltene model and showed that $V_{m,a}$ increases linearly with temperature, thus leading to a decrease in δ_a . These trends were also reported by Hirschberg et al. (1984). The effect on the mixture solubility parameter, however, should be minimal as it is dominated by the high solvent and precipitant volumes.

To confirm the viability of approach 2, the mixture solubility parameter for the heptane experiments at $T = 298$ K was calculated using the heat of vaporisation at

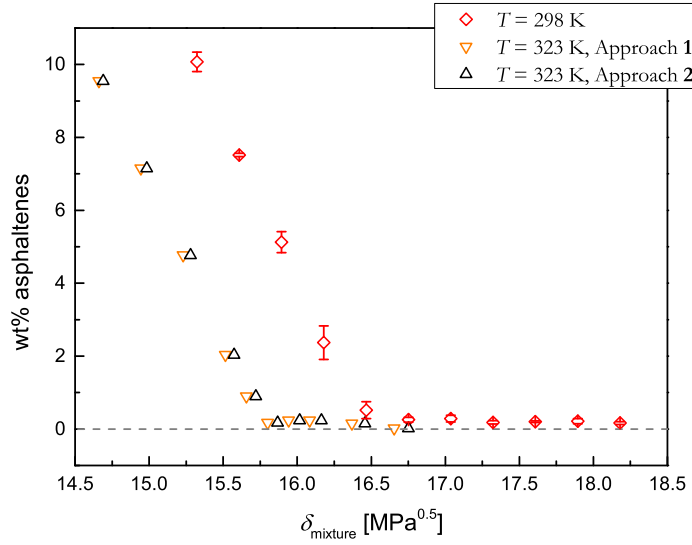


Figure 3.9: Asphaltene precipitation from a crude oil+heptol mixture at different temperatures with mixture solubility parameters estimated by the two approaches described in the text.

that temperature. Table 3.8 compares δ_i calculated from approach 2 and with the linear relationship (Equation (3.1)).

Table 3.8: Solubility parameters of heptane and toluene at $T = 298 \text{ K}$. The values in the first column were calculated by applying the linear relationship in Equation (3.1) by Buckley and Wang (2002) and the values in the second column from Equation (3.8). *Note: The crude oil solubility parameter remained as before ($\delta_{\text{oil}} = 19.96 \text{ MPa}^{0.5}$).*

δ_i	Equation (3.1)	Equation (3.8)
Toluene	18.14	18.28
Heptane	15.21	15.26

Figure 3.10 compares the results in terms of the mixture solubility parameter, with a percentage difference of 0.48% at the onset point, which is within the error margin ($0.13 \text{ MPa}^{0.5}$). Approach 2, therefore, gives consistent results and for the rest of the work, this approach is used to calculate the mixture solubility parameter

at $T = 323$ K.

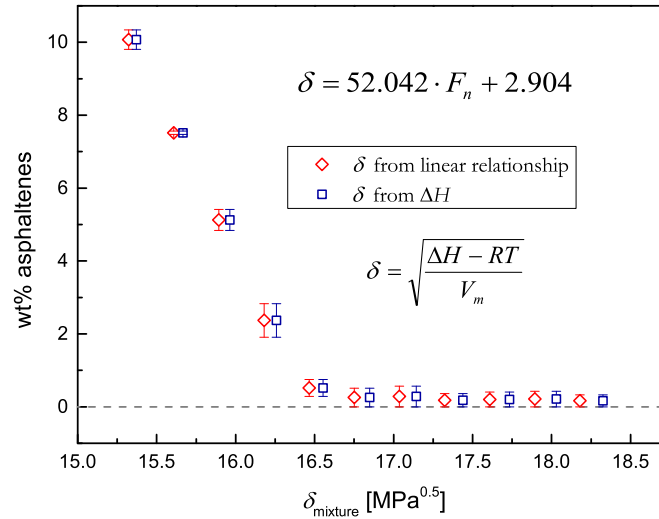


Figure 3.10: Asphaltene precipitation at ambient conditions comparing the linear relationship by Buckley and Wang (2002) and approach 2 to calculate δ_{mixture} .

3.3.3 Filtration Experiments at HPHT

Precipitation induced by CO₂ was studied for the original crude oil and a diluted version (70wt% oil+30wt% toluene) at $T = 323$ K as a function of applied pressure in the filtration cell, shown in Figure 3.11. In a pressure range from 30 - 80 bar no asphaltenes were found on the filter paper. The precipitation onset point lies within a pressure range of $p = 80 - 100$ bar. Beyond the onset point the increase of asphaltenes mass follows a similar trend to the hydrocarbon experiments: It increases linearly with increasing pressure. Fewer data points were taken for the original crude oil which was associated with the increased difficulty in handling the experimental apparatus. Regardless, the trend observed seems reliable and comparable to the diluted crude oil. A notable difference, however, is that more asphaltenes precipitate from the original crude oil at a given pressure.

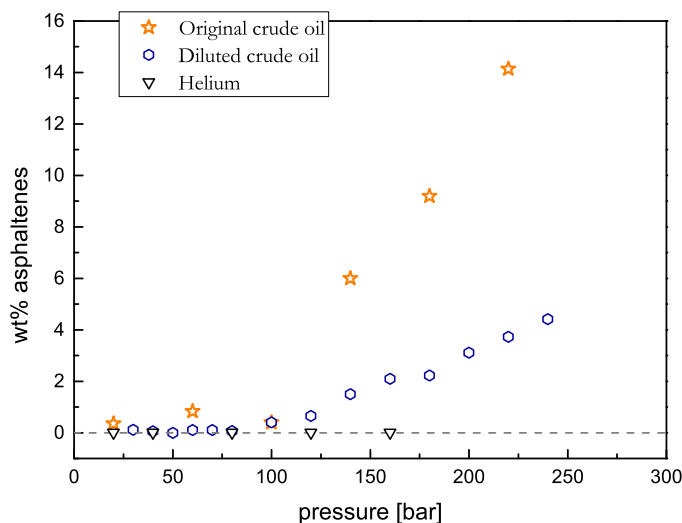


Figure 3.11: Asphaltene precipitation with CO_2 from the original and diluted crude oil, compared to Helium experiments at different system pressures at $T = 323$ K.

To distinguish the effects of pressure separately from the effects of the dissolved CO_2 , the diluted crude oil was pressurised with Helium which is almost insoluble in oil. Helium did not initiate asphaltene precipitation within the pressure range ($p = 30 - 160$ bar) investigated (Figure 3.11). These results are expected for a dead crude oil as pressurising the crude oil should not alter the composition when no additional soluble component is present.

Figure 3.12 shows a photograph of the filter paper and precipitated asphaltenes, taken after the corresponding experiment. The asphaltenes precipitated with heptane are a black powder, whereas the CO_2 -asphaltenes are stickier and shinier. These two types are probably different in physical and chemical nature, hence the different appearance. Additionally, the CO_2 precipitated asphaltenes were not washed after filtration. The filter paper on the right shows the oil residue after pressurising the cell with Helium at $T = 323$ K and $p = 140$ bar, confirming the conclusion drawn from Figure 3.11, that Helium does not initiate asphaltene precipitation at

the system pressure range investigated.



Figure 3.12: Precipitated asphaltenes after the experiments: C7-asphaltenes at ambient conditions and after drying in the oven (left), CO₂-asphaltenes precipitated at $T = 323$ K and $p = 200$ bar on the filter paper along with residual oil (middle), residue on the filter paper after HPHT experiments ($T = 323$ K, $p = 140$ bar) with diluted crude oil and Helium (right).

3.3.4 Solubility of CO₂ in Crude Oil

The following experiments were carried out by Ruien Hu. A more detailed description about the experimental set-up and the results can be found in Seifried et al. (2015), Hu et al. (2016), and Hu (2016). The data presented here are used in later analysis.

To further investigate the effect of CO₂ on asphaltene precipitation, the mass fraction of CO₂ (w_{CO_2}) soluble in the diluted and original crude oil was measured. The measurement principle was as follows: A known amount of crude oil was first loaded into a mixer. After vacuuming the system, the mixer was heated up to the desired temperature ($T = 323$ K). CO₂ was then introduced into the mixer via a

syringe pump. The bottom of the mixer contained a stirrer coupled with a rotating magnet, which was subsequently used to enhance the mixing between crude oil and CO_2 . Therefore, most of the CO_2 dissolution into crude oil is caused by stirring only. The syringe pump was set to operate at constant pressure mode and when the pressure stabilised at the desired level, the stirrer was turned on to start the mixing. The rapid dissolution of CO_2 in the oil results in a volume change in the syringe pump which then allows for determining the mass of dissolved CO_2 . The error bars were estimated from the volume fluctuations in the syringe pump during the experiments.

Figure 3.13a and Figure 3.13b show the phase diagram in the form of a pressure-composition isotherm for the diluted and original crude oil, respectively. Both diagrams show partially the phase envelope, inside which two phases exist (liquid (L) and vapour (V)). This region is bounded by the bubble curve, here separating the two phase region from the single liquid phase occurring at higher pressure. The drastic change in slope at $p = 100$ bar, seen in Figure 3.13a, is indicative of a three phase region where the mixture exhibits liquid-liquid immiscibility, likely due to asphaltene precipitation. A comparable behaviour can be observed in Figure 3.13b, where the VL boundary is assumed to occur almost horizontal above $p = 100$ bar. Similar phase diagrams of bitumen+ CO_2 mixtures were produced by Mehrotra and Svrcek (1985), where the authors attributed a change in slope to the existence of a LL region.

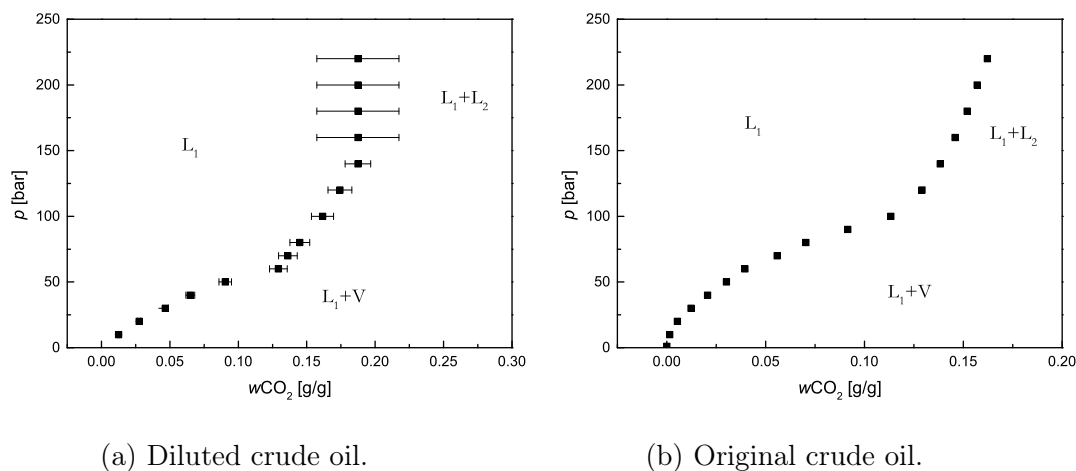


Figure 3.13: CO₂+crude oil phase diagram at $T = 323$ K.

3.3.5 The Solubility Parameter Approach

A common approach to understand the state of asphaltenes in crude oil is to study the system solubility parameter as asphaltenes are defined as a solubility class. The concept of the solubility parameter has been proven to successfully describe the asphaltene precipitation comparing light hydrocarbons, as shown above. The following section discusses the extension of this approach to the supercritical CO₂ experiments.

The previously used linear mixing rule offers an accurate estimation of the mixture solubility parameter for liquid hydrocarbons at constant pressure and temperature. However, when dissolved CO₂ is present at high pressure, special treatment of that rule is required. Using the geometric mean for the intermolecular forces among oil and CO₂ is no longer valid, as compressibility, swelling and the change in molar volume with pressure are not taken into account.

A different approach can then be followed by defining the volume fraction in

terms of the mole fraction and the partial molar volume of component i :

$$V_{m,mixture} = \sum_i x_i V_{m,i} \quad (3.11)$$

where, $V_{m,mixture}$ = molar volume of the mixture

The mole fraction of CO_2 can be calculated from the weight fraction of CO_2 soluble in the crude oil (w_{CO_2}) using the following approach:

$$\begin{aligned} x_{CO_2} &= \frac{n_{CO_2}}{n_{CO_2} + n_{oil}} \\ &= \frac{\frac{m_{CO_2}}{M_{CO_2}}}{\frac{m_{CO_2}}{M_{CO_2}} + \frac{m_{oil}}{M_{oil}}} \\ &= \frac{\frac{w_{CO_2} \times m_{TOTAL}}{M_{CO_2}}}{\frac{w_{CO_2} \times m_{TOTAL}}{M_{CO_2}} + \frac{(1 - w_{CO_2})m_{TOTAL}}{M_{oil}}} \\ &= w_{CO_2} \frac{M_{oil}}{M_{oil} \times w_{CO_2} + M_{CO_2}(1 - w_{CO_2})} \end{aligned} \quad (3.12)$$

The mole fraction of crude oil can therefore be obtained through $x_{oil} = (1 - x_{CO_2})$.

Combining the original mixing rule with the modification yields:

$$\delta'_{mixture} = \sum_i \varphi'_i \delta_i \quad (3.13)$$

Where,

$$\varphi'_i = x_i \frac{V_{m,i}}{V_{m,mixture}} \quad (3.14)$$

This approach was only considered for the original crude oil+CO₂ mixture, as the fraction of CO₂ in the diluted crude oil cannot satisfactorily be estimated due to the complex phase behaviour. According to Figure 3.13a the mass fraction eventually reaches steady state, which by combining with the pure CO₂ density, would result in a decrease in volume fraction of CO₂ soluble in the oil (Figure 3.14); a behaviour which does not reconcile with the mixing rule. A more detailed discussion about the usability of the pure component density is presented below.

The thermophysical data, required to calculate δ_{CO_2} at $T = 323$ K with Equation (3.4), were taken from NIST and are shown along with δ_{CO_2} in Table A.15. The change of δ_{CO_2} with pressure is displayed in Figure 3.15.

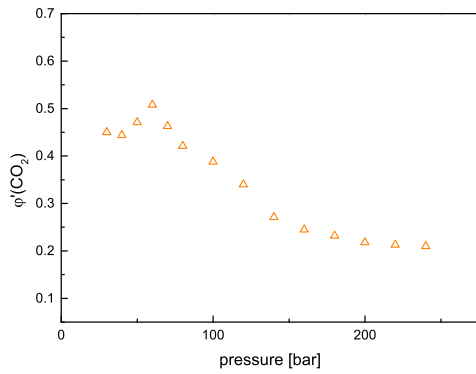


Figure 3.14: Volume fraction of CO₂ soluble in the diluted crude oil, taken from Figure 3.13a.

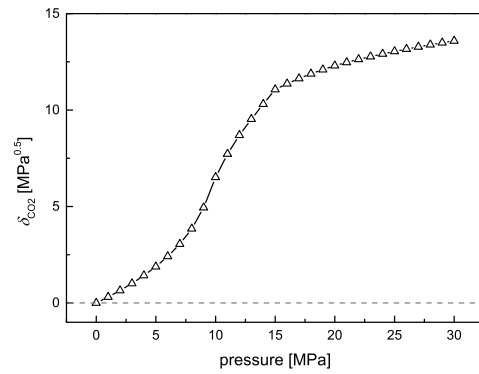


Figure 3.15: Increasing solubility parameter δ_{CO_2} with pressure according to Allada (1984) at $T = 323$ K.

Table A.16 shows the mixture solubility parameters for the original crude oil+CO₂ mixture at the pressure range investigated. The crude oil density was estimated from

a density-pressure correlation for decane given in Caudwell et al. (2008). The results are compared to the heptane experiments in Figure 3.16, where the calculation of δ_{mixture} for the crude oil+heptol mixture remained the same as described above.

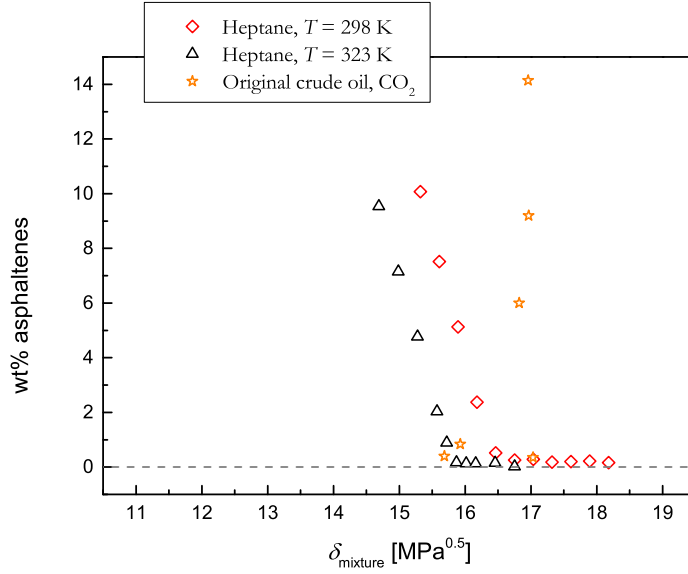


Figure 3.16: Asphaltene precipitation from the original crude oil with CO_2 , compared to heptane induced precipitation at $T = 298 \text{ K}$ and $T = 323 \text{ K}$ in terms of the mixture solubility parameter δ_{mixture} .

The initial behaviour before precipitation and the onset point can be described precisely by the solubility parameter concept. However, beyond that the asphaltene mass increases with increasing mixture solubility parameter, which seems counter-intuitive: As asphaltenes are defined as a solubility class, their behaviour will change in a different solvent environment. The Flory-Huggins interaction parameter χ describes the stability of polymer solution, but it appears to work well for liquid hydrocarbon+asphaltene mixtures. The dimensionless Flory-Huggins parameter is defined by Equation (3.15):

$$\chi = \frac{V_{\text{m,mixture}}}{RT} (\delta_{\text{asphaltenes}} - \delta_{\text{mixture}})^2 \quad (3.15)$$

It characterizes the differences of interaction energy between the solvent and the solute (here: asphaltenes) with those between the pure components. A solute which has a similar solubility parameter as the solvent tends to be more compatible and the value for χ decreases. A smaller χ indicates a more miscible environment for the asphaltenes in the crude oil+solvent+precipitant mixture. Figure 3.16, however, suggests that an increasing mixture solubility parameter, hence a smaller χ , favours phase separation (here: asphaltene precipitation). A second region of asphaltene precipitation would be expected at very high values of the mixture solubility parameter, but only above the asphaltene solubility parameter, which ranges usually between 20-23 MPa^{0.5} (Hirschberg et al. 1984; Wang et al. 2010).

Possible reasons for the deviation of the mixture solubility parameter within the precipitation regime are listed below:

- The mass fraction of CO₂ soluble in the heavy crude oil increases with pressure according to Figure 3.13b. In combination with the increasing pure CO₂ density with pressure (Table A.15), the volume fraction of CO₂ eventually levels off. This, finally, leads to an almost constant mixture solubility parameter in the precipitation regime. However, δ_{mixture} cannot be estimated using only the pure component density values, as the extent of density change with pressure is unknown when the oil+CO₂ mixture reaches equilibrium. Upon reaching saturation, the density of the mixture increases due to pressure, counter-balanced by a density reduction with increased swelling and solubility. Instead the effective density should be used or it needs to be accounted for the excess volume of mixing.
- At high pressure, partial crude oil extraction into the CO₂ rich phase might have occurred.

- The Hildebrand solubility parameter theory was developed on the assumption that the dominant interactions governing aggregation and precipitation are London dispersion forces. The dominance of London dispersion forces would not be true if a major amount of polar components were added to the crude oil. Buckley et al. (1998) stated that the polar components are not significant compared to the amount of non-polar hydrocarbons present in the crude oil, thus this contribution can be ignored. However, CO₂ possesses a quadruple moment, displaying Lewis acid-base characteristics. According to Williams et al. (2004), the polar and hydrogen-binding contributions to the solubility parameter model cannot be ignored. If these components differences were quantitatively taking into account in the solubility theory, predicting asphaltene solubility may become more accurate.

3.3.6 Phase Behaviour of a Crude Oil Model

A detailed understanding and description of crude oil and asphaltene behaviour is an experimental and theoretical challenge and asphaltenes are far from being precisely characterised. Crude oil is such a complex mixture that describing each individual component is not feasible. Describing the phase behaviour by lumping together components is therefore a common practice, thus decreasing the complexity of the multi-component system (Artola et al. 2011). The following section will address the fluid phase behaviour by choosing a simplified model of the Zuata crude oil. Asphaltene precipitation will be determined here by a liquid-liquid phase separation as fluid de-mixing occurs due to the addition of aliphatic components.

3.3.6.1 Crude Oil + 0.1 mol% PS9

Figure 3.17 shows the p - T envelope of the model crude oil + 0.1mol% of PS9. The phase behaviour shows a liquid-liquid critical line at low temperature ($T = 242$ K).

The mixture is non-miscible in this temperature region, consequently a LLE line appears. The LLE runs to infinite pressure, as that property method doesn't account for solids. The next limit of phase equilibrium region appears with increasing temperature indicated by a continuous liquid-vapour curve. The existence of a bubble curve is similar to the phase diagram of a binary system (Artola et al. 2011). At even higher temperature a three-phase region is observed which decreases with increasing pressure. On entering the VLLE region, one liquid phase contains most of the PS9 molecules and the second liquid phase contains the lighter components and almost no "asphaltenes". The VLLE boundary is indicative of asphaltene precipitation.

The distribution of PS9 in the different phases is further highlighted in Figure 3.18. At low temperature one phase exists in the LE region and with increasing temperature partial evaporation occurs, transferring an extremely small fraction of PS9 into the vapour phase. At $T = 622$ K a third phase appears, creating an "asphaltenes" rich phase. At higher temperature once more two phases are observed, with an "asphaltene" rich phase and with almost six order of magnitudes smaller fraction remaining in the vapour phase.

3.3.6.2 Crude Oil + 0.1 mol% PS9 + C7

Adding another component to the mixture, in this case heptane (C7), can be seen as an analogue to the addition of a precipitant. The diagram in Figure 3.19 is qualitatively similar to the previous one, however with an expanded VLLE region, suggesting that addition of another hydrocarbon introduces instabilities at lower temperature in terms of the precipitation boundary and that "asphaltenes" solubility decreases with increasing temperature.

The effect of adding another component is also shown in Figure 3.20 for a given temperature range at a constant pressure of $p = 0.5$ MPa, where C7 was gradually added to the crude oil model, while keeping the PS9 fraction constant at 0.1

mol%. Figure 3.20 also considers the effect of increasing the molecular weight of PS by adding more segments to the oligomer (PS12). With this increasing degree of asymmetry, the system becomes less miscible at lower temperature, while the bubble curve remains unchanged.

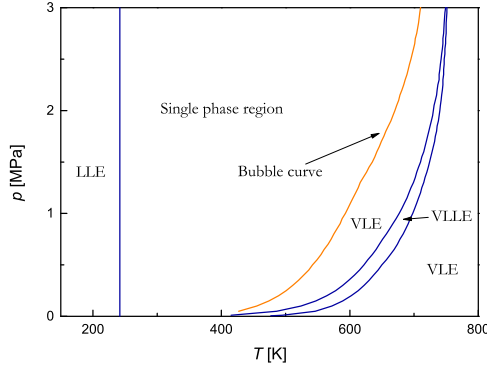


Figure 3.17: p - T phase diagram of the crude oil model at constant composition. *Note: A solid phase is not considered here.*

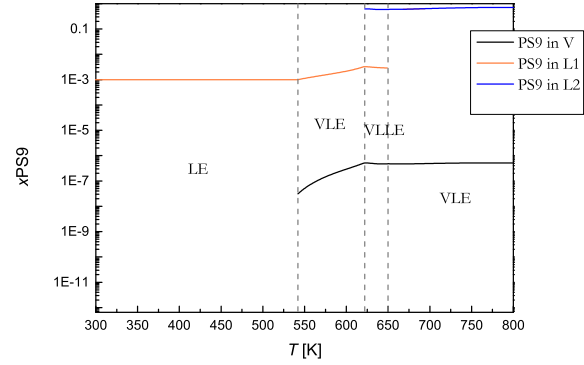


Figure 3.18: Change of composition x_{PS9} in the different phases at $p = 0.5$ MPa. The dashed vertical lines show the phase boundaries.

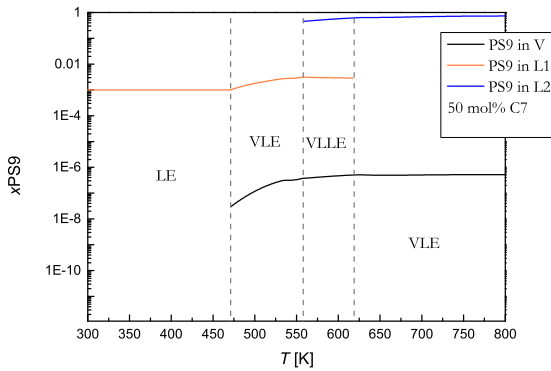


Figure 3.19: Change of composition x_{PS9} with 50mol% C7 added to the crude oil in the different phases at $p = 0.5$ MPa.

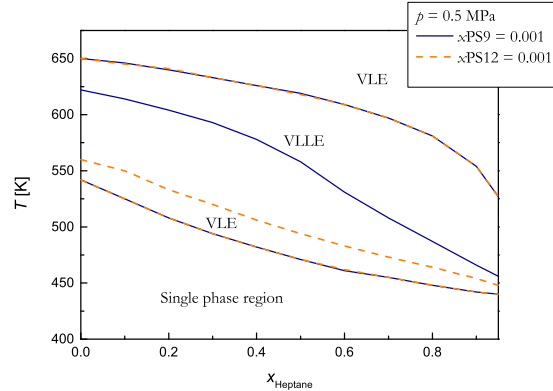


Figure 3.20: Isobaric ($p = 0.5$ MPa) temperature composition (T - x) phase diagram for the crude oil model (PS9 and PS12)+C7 system.

3.4 Chapter Conclusions

The results obtained here will help to understand asphaltene behaviour in EOR operations in more detail as it is yet not fully identified how heavy crude oil asphaltenes behave under precipitating conditions. For three different light hydrocarbons a common precipitation onset point was identified in terms of the Hildebrand solubility parameter. Temperature effects on asphaltene precipitation with the same precipitant requires further investigation with regards to the usefulness of the solubility parameter, even though it was shown that the precipitation mechanism seems to be independent of the temperature. For the first time, asphaltene precipitation with CO₂ was combined with an estimated mass of CO₂ dissolved in crude oil under conditions where the assumption of full miscibility is not valid. Reconciling the data, by revising the mixing rule in the solubility parameter approach, established a dependence on the change in molar volume of the components and compressibility effects when gaseous or supercritical CO₂ was mixed with crude oil. It is believed that the effect of composition changes and pressure on asphaltenes precipitation is generally stronger than the effect of temperature.

The experimental work was qualitatively supported from a thermodynamic perspective by using a simplified crude oil model, restricted to only four components and showing the underlying physics governing the phase equilibria. The bubble curve represents a boundary between a stable region and liquid-liquid de-mixing, indicative for precipitation. Qualitatively, the precipitation boundary was captured successfully relating these events to precipitation. It was shown that changing the oil composition by introducing light hydrocarbons introduces instabilities, which is agreement with the experimental findings. A better quantitative agreement with the experiments can be achieved by further improving the asphaltene molecule in the model. A pseudo-component could be defined by tweaking the parameters for

PS9 or by building a molecular architecture around a more realistic component. This could be achieved by introducing polydispersity due to a variation of polymers possessing a different molar mass.

Chapter 4

Asphaltene Deposition in Capillary Flow

4.1 Introduction

Capillary flow experiments are a widely used tool to evaluate asphaltene deposition. Despite a relatively simple experimental methodology, which involves co-injecting a fluid containing asphaltenes in solution and a precipitant at constant flow rate while measuring the pressure drop across the capillary, asphaltene deposition at various conditions is yet not well understood. Previous deposition studies have focused only on the transient pressure drop profiles to compare them to variations in experimental conditions such as the effect of type of precipitant (Wang et al. 2004; Lawal et al. 2012).

The work presented in the following chapter builds on the work of Boek et al. (2008) and Boek et al. (2010), where capillary flow experiments were compared to computer simulations. Even though a good comparison was found and the experimental pressure drop data were successfully used to describe the deposition behaviour, a wide variation in the experimental data with regards to reproducibility

were found. Here, the same experimental conditions are applied to investigate the effect of several parameters on asphaltene deposition on the capillary wall. Based on the theory by Nabzar and Aguiléra (2008), different deposition regimes can be identified with a change in shear rate (Section 2.4.3). These events are discussed here, by investigating a wider range of flow rates within the Stokes flow regime ($Re \approx 1$). The variation in asphaltene aggregate size, caused by a balance between floc break-up and collision depending on shear, is believed to have an effect on the deposition kinetics. Therefore, different floc sizes are produced in a Couette mixer and then subsequently analysed with Dynamic Light Scattering. These findings are compared to SRD computer simulation and to visual observation of the asphaltene deposits by confocal laser-scanning microscopy. This chapter concludes then with a discussion about the axial deposition profile along the capillary, where the results obtained here are compared to a homogeneous deposition model (Papanastasiou et al. 1999).

4.2 Materials and Methodology

4.2.1 Experimental Set-up

The experimental set-up for the capillary flow experiments is illustrated in Figure 4.1 and Figure 4.2. Due to the high crude oil viscosity and to keep the asphaltene concentration at approximately 1 g/L, 0.983 g of crude oil were mixed with 110 mL of toluene (Boek et al. 2010). The equipment consisted of two constant-rate syringe pumps (BS-800, Braintree Scientific, U.S.) for the precipitant and crude oil+solvent stream, respectively. The fluids were co-injected into the glass capillary using two Hamilton syringes (1010LT, Sigma-Aldrich, U.K.).

The asphaltene deposition was studied in a rectangular borosilicate glass capillary (VD/5005-100, Camlab Ltd., U.K.). The capillary was 100 mm long, 600 μm



Figure 4.1: Experimental set-up for the capillary flow experiments (photograph). 1, 1a = syringe pumps; 2 = heptane in the Hamilton syringe; 3 = crude oil+toluene mixture in the Hamilton syringe; 4 = glass capillary and metal holder; 5 = pressure transducer and data acquisition system; 6 = petridish filled with water; 7 = magnetic stirrer.

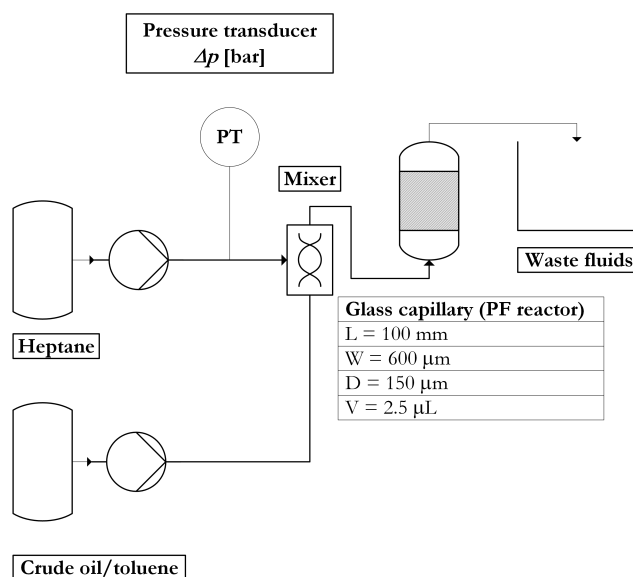


Figure 4.2: Experimental set-up for the capillary flow experiments (schematic diagram). The function of the mixer displayed above will be explained in a later section.

wide, thus having a slot dimension of $50 \times 500 \mu\text{m}$, a volume of $2.5 \mu\text{L}$ and a cross section of $2.5 \times 10^{-8} \text{ m}^2$. The glass capillary was inserted into a PEEK Y-connector (P-512, Kinesis, U.K.) and subsequently mounted on a metal holder (Mechanical Workshop, Department of Chemical Engineering, Imperial College London) with a plain microscope slide (L-4244, Agar Scientific). The gap in between the capillary and one ending of the Y-connector was sealed using ARALDITE glue and left to set for one hour at room temperature before the assembly was used in the experiment. The Y-connector and the syringes were connected via fittings (XP-235X, Kinesis, U.K.), plastic tubings and adapters (P-629, Kinesis, U.K.). For each run, a new capillary was used and the crude oil+toluene line was cleaned with toluene and dried at room temperature. The change in pressure was recorded as a function of time in steps of 10 seconds, using the data logger “Windmill, v6.0” and with the aid of a pressure transducer (6 bar g, 0.5 V, PMP 1400). The pressure transducer was connected between the precipitant syringe pump and the capillary using a T-connector (P-727, Kinesis, U.K.). The fluids were set at constant flow rate, giving a fixed heptane to diluted crude oil ratio and injected through the capillary. The outgoing fluids and precipitated, but not deposited, asphaltenes were collected in a petridish filled with water, which was stirred using a magnetic stirrer. By allowing the end of the tilted capillary to be dipped into water, the evaporation of toluene was avoided, which may have caused blocking of the capillary with asphaltenes, while avoiding water imbibition into the capillary. All experiments described in this chapter were carried out at ambient conditions.

The Choice of Flow Rates To obtain an optimal design for the experiments and to ensure that the chosen flow rates were in the regime of flow in porous media, the dimensionless numbers Peclet $Pe^{\text{flow}} \gg 1$ (hydrodynamic interactions are more important than Brownian motion) and Reynolds $Re \approx 1$ (Stokes flow, where inertial

effects are negligible) were used. The Reynolds number (Re) is a measure of inertial over viscous forces in a fluid flow and is expressed as follows:

$$Re = \frac{v^{\text{flow}} a_p \rho}{\mu} \quad (4.1)$$

where, v_{flow} = flow velocity; a_p = length scale (here: diameter of asphaltene colloids); μ = kinematic viscosity; ρ = fluid density

The Peclet number (Pe) is defined as the ratio of advective to diffusive transport:

$$Pe = \frac{v^{\text{flow}} a_p}{D} \quad (4.2)$$

where, D = diffusion coefficient

Where,

$$D = \frac{k_B T}{6\pi\mu r} \quad (4.3)$$

where, k_B = boltzmann constant; T = temperature; r = radius of an asphaltene colloid [3 μm (Boek et al. 2010)]

The fluid viscosity of the diluted crude oil+heptane mixture was measured in a rheometer (Anton Paar MCR301, Germany) at ambient conditions in two independent consecutive runs. The mixture density was averaged from the density of the pure component ρ_i and the volume fraction of the individual component φ_i according to Equation (4.4):

$$\rho_{\text{mixture}} = \sum_i \varphi_i \rho_i \quad (4.4)$$

The diffusion coefficient D was calculated with the Stokes-Einstein relationship

(Equation (4.3)). Listed below are all the calculated fluid properties needed to calculate Re and Pe :

■ $\mu_{\text{mixture}} = 0.895 \pm 0.015 \text{ mPa}\cdot\text{s}.$

■ $\rho_{\text{mixture}} \approx 700 \text{ kg/m}^3$

■ $D = 8.17 \times 10^{-14} \text{ m}^2/\text{s}$

Table 4.1 summarizes the chosen total volumetric flow rates Q_t and the corresponding dimensionless numbers.

Table 4.1: Volumetric flow rates, linear velocities and calculated dimensionless numbers Re and Pe for the capillary flow experiments.

Flow rate Q_t [$\mu\text{L}/\text{min}$]	Flow rate Q_t [m^3/s]	Linear velocity v^{flow} [m/s]	Re	Pe
2	3.33×10^{-11}	0.04	0.10	1.62×10^6
5	8.33×10^{-11}	0.11	0.26	4.04×10^6
7	1.17×10^{-10}	0.15	0.35	5.51×10^6
10	1.67×10^{-10}	0.22	0.52	8.08×10^6
12	2.00×10^{-10}	0.26	0.61	9.55×10^6
25	4.17×10^{-10}	0.55	1.30	2.02×10^7
60	1.00×10^{-9}	1.32	3.11	4.85×10^7
80	1.33×10^{-9}	1.76	4.15	4.46×10^7

4.2.2 Confocal Laser-Scanning Microscopy (CLSM) Imaging

A first step towards understanding asphaltene deposition in capillary flow is to image the capillary after the deposition experiment at steady pressure. For that purpose, a confocal laser-scanning microscope (CLSM) LSM 700 (Carl Zeiss, Germany) was used.

An image of the CLSM is displayed in Figure 4.3, where the most important parts of the microscope are highlighted. The microscope contains three continuously

emitting lasers with different excitation wavelengths. The intensity of each laser can be varied individually and are mounted on a laser combiner and coupled into a scanning module through optical fibres with an integrating filter. Using this filter, the desired wavelength can be chosen. The properties of each laser are shown in Table 4.2.

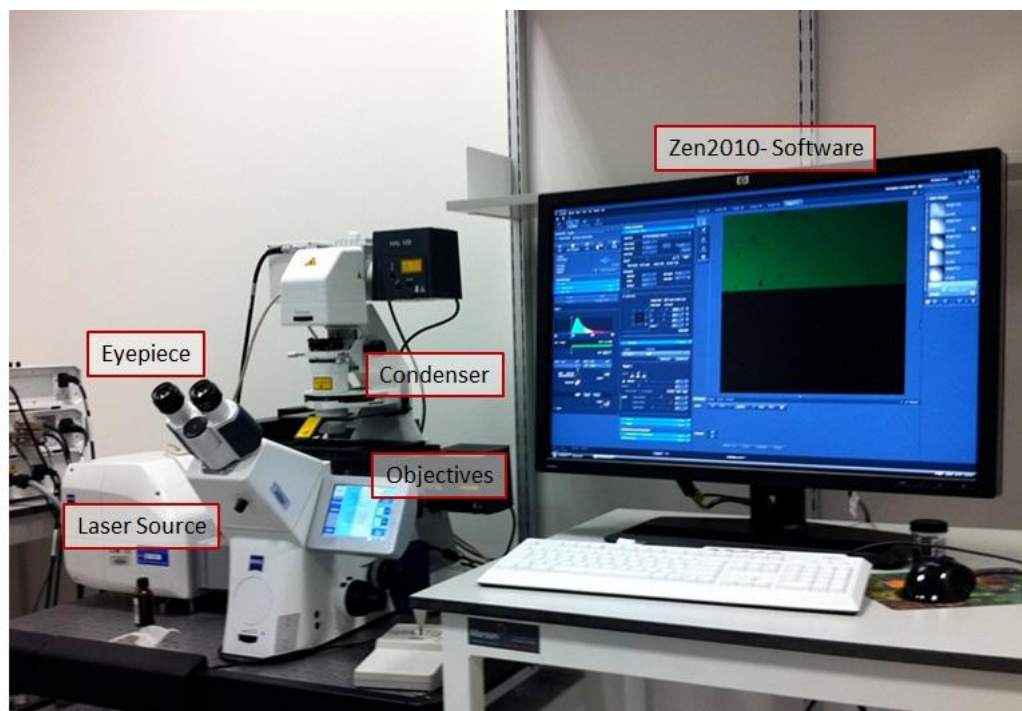


Figure 4.3: CLSM set-up.

Table 4.2: Available CLSM laser types.

Laser type	Wavelength [nm]	Power [mW]
V/VIS PTC Argon-laser (purple)	405	5
V/VIS PTC Argon-laser (blue)	488	10
V/VIS PTC laser (green)	555	10

With two independent galvanometric scanning mirrors, the laser light is directed through the objective lens and then on to the sample, which is scanned by the laser

beam in a point-by-point mode. A joystick supports the control of the x/y -scanning stage. A EC Plan-Neofluar ($10\times$) objective lens ($N.A. = 0.3$, immersion-medium = air) in transmission mode was used to image the capillary. The confocal plane can be adjusted by moving the objective lens holder using the focus wheel. The scan resolution and speed (up to 26 speed levels) are continuously adjustable by the software (Zen 2010). The light transmitted through the sample is then detected by two detectors. Different imaging modules were available, however only the main one used to image the capillaries is shown in Figure 4.4. With the **Tile Scan** module a fast overview of the specimen can be obtained. It captures a mosaic of several images with a motorized x/y -scanning motor. Areas of interest can quickly be identified.

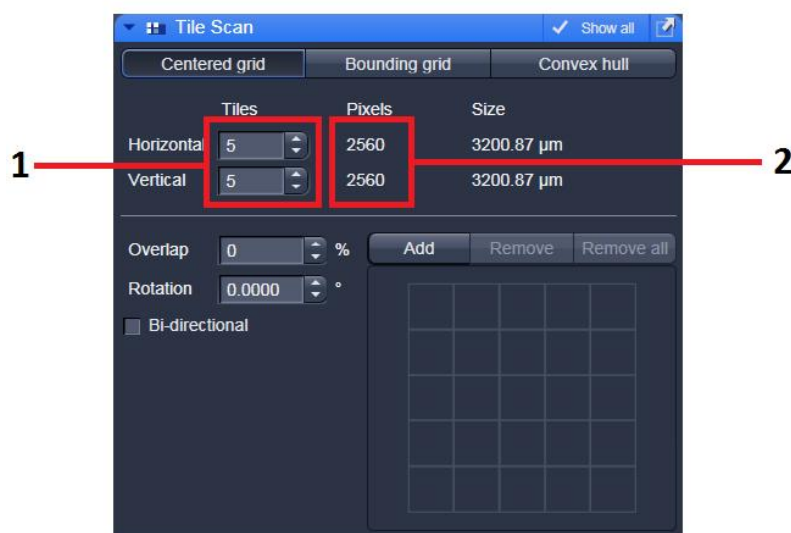


Figure 4.4: CLSM tile scan module. 1 = number of slices in horizontal and vertical direction; 2 = number of pixels

Figure 4.5 shows an example of the capabilities of the CLSM, where asphaltene aggregates were scanned in *in-situ* experiments in heptol. Further details can be found in Seifried et al. (2013b). The confocal image was taken with the Plan Apochromat DIC M27 ($63\times$) objective lens (numerical aperture $N.A. = 1.4$, immersion-medium = oil) in transmission mode.

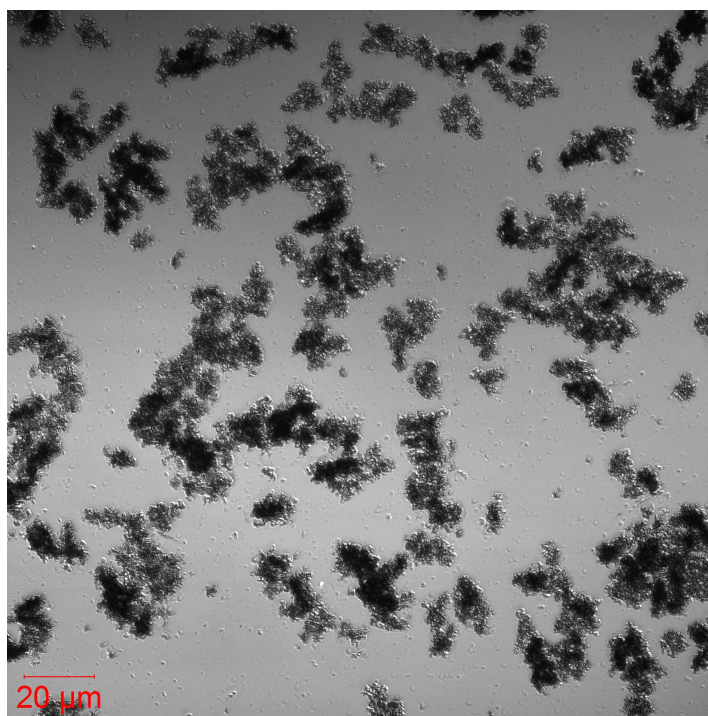


Figure 4.5: Example of an asphaltene aggregate in heptol. Structural information is clearly revealed using the confocal principle (Seifried et al. 2013b).

4.2.3 Design of the Couette Mixer

A Couette mixer has been designed with the purpose of measuring the asphaltene aggregate size with changing shear rate and different reaction times, corresponding to the experimental conditions in the capillary flow experiments. Thus, the Couette device was operated at controlled laminar flow. After initiating precipitation and aggregation in the mixer, the average particle size was analysed with Dynamic Light Scattering (DLS) (described below). It was decided to design and build the mixer *in-house* (Design: C.M. Seifried, Fabrication: Mechanical Workshop, Department of Chemical Engineering, Imperial College London) in order to achieve the desired shear rates, ensuring sufficient volume to be measured in the DLS, while at the same time keeping the device small and portable to minimise the time in between mixing

and sample transferring.

Several requirements have to be met to achieve the optimal design:

- The applied **shear rate** should be comparable to the volumetric flow rates in the capillary flow experiments.
- The **mixing time** should be comparable to the residence time in the capillary flow experiments.
- To avoid secondary flow and Taylor vortices, the **Taylor number** (Ta) should be below the critical Taylor number.

The average shear rate in the capillary is calculated using:

$$\dot{\gamma}_{av.} = \frac{3Q_t}{8a^2b} \quad (4.5)$$

where, $\dot{\gamma}_{av.}$ = average shear rate; Q_t = volumetric flow rate; a = half capillary depth (= 25 μm); b = half capillary width (= 250 μm)

The calculated shear rates are converted into velocity and subsequently into stirrer speed as per below. The EUROSTAR power-b (IKA Werke) stirrer can be operated between 50 and 2000 rpm. To obtain stirrer speeds within that range, the velocity can be chosen accordingly by adjusting the diameter of the mixer and the gap width between the inner and the outer cylinder.

$$\begin{aligned} \dot{\gamma} &= \frac{v}{h} \\ \therefore v &= \dot{\gamma} \times h \end{aligned} \quad (4.6)$$

where, h = gap width (= 0.55 mm); v = velocity

$$rpm = \frac{v}{\pi d_{\text{Couette}}} \quad (4.7)$$

where, rpm = rotational stirrer speed; d_{Couette} = mixer diameter (= 42 mm)

The final design of the mixer is shown in Figure 4.6. By choosing the gap width h to be much smaller than the inner Couette diameter, a constant velocity gradient across the gap is achieved. To obtain the optimal design according to the above criteria, the inner cylinder has a diameter of 40.90 mm and the outer cylinder has an inner diameter of 42 mm. This leaves an annular gap width of 0.55 mm. The outer cylinder is fixed, while the rotational speed of the inner one can be adjusted using the stirrer. The axis of the rotor was fixed by allowing it to be stabilised in a cavity at the bottom of the outer cylinder. With this set-up it was ensured that the gap width remained constant during the experiment.



Figure 4.6: Photograph of the designed Couette mixer. The inner cylinder is attached to the stirrer and the fluids are injected and released through the plastic tubing.

To ensure controlled laminar flow, both turbulence and inertial instabilities have

to be avoided. Therefore, the dimensionless Taylor number (Ta) was used to ensure that the flow regime is below the critical Taylor number ($Ta < Ta_{cr}$, where $Ta_{cr} \approx 1700$). The Taylor number was calculated with the previously chosen reactor dimensions and stirrer speeds (Equation (4.8)).

$$Ta = \frac{\Omega^2 r_1 (r_2 - r_1)^3}{\nu^2} \quad (4.8)$$

where, Ta = Taylor number; Ω = angular velocity of the inner cylinder [rad/s]; r_1 = external radius of the internal cylinder (= 20.45 mm); r_2 = internal radius of the external cylinder (= 21 mm); ν = kinematic viscosity of the fluid mixture ($= 1.26 \times 10^{-6} \text{ m}^2/\text{s}$)

The mixing time was set equal to the residence time τ in the capillary flow experiments:

$$\tau = \frac{V}{Q_t} \quad (4.9)$$

where, τ = residence time; V = capillary volume (= 2.5 μL)

Table 4.3 summarises the stirrer speeds which were used in the experiments according to the criteria mentioned above. The values highlighted in bold were not used as they are either below the minimum stirrer speed or above the critical Taylor number. To precipitate and aggregate the asphaltenes in the mixer, a constant volume of the diluted crude oil in toluene was mixed with heptane in a ratio of oil to heptane 1 : 3. Immediately upon mixing the fluid mixture was injected into the cell and left to equilibrate for a given amount of time and at the desired stirrer speed.

Table 4.3: Calculated stirrer speed, capillary flow residence times τ and Ta numbers for the Couette flow device studies. The volumetric flow rates used in the capillary flow experiments were converted into shear rate, velocity and subsequently stirrer speed (rpm).

Flow rate Q_t [$\mu\text{L}/\text{min}$]	$\dot{\gamma}_{av.}$ [s^{-1}]	Velocity v [m/min]	rpm [min^{-1}]	Ta	τ [s]
2	80	2.64	20.01	9.45	75.0
5	200	6.60	50.02	59.08	30.0
7	280	9.24	70.03	115.79	21.4
10	400	13.20	100.04	236.31	15.0
12	480	15.84	120.05	340.28	12.5
25	1000	33.00	250.10	1476.91	6.0
60	2400	79.20	600.24	8507.01	2.5
80	3200	105.60	800.32	15123.57	1.9

4.2.4 Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) was used to measure the average asphaltene aggregate size as a function of time and shear rate after asphaltene precipitation upon mixing crude oil and heptane in the Couette flow mixer. In this section, firstly a brief introduction to the DLS method is given, followed by a description about the sample preparation and data analysis. Lastly, the difficulties in using DLS for a crude oil sample are discussed.

Introducing DLS DLS is a non-invasive technique to measure the size and size distribution of particles and/or droplets, typically in the sub-micron region. The size distribution is obtained from measuring the light scattered by the particles, which diffuse through the solution due to Brownian motion. DLS then measures the speed of molecules undergoing Brownian motion, which is influenced by particle size, sample velocity and temperature. Smaller particles experience a more rapid Brownian motion through the sample and this velocity is then converted to the

Stokes-Einstein relationship (Equation (4.3)). Smaller particles show a more rapid intensity fluctuations over time due to their higher speed through the sample (Figure 4.7). In a DLS measurement, a so called time autocorrelation function $G(\xi)$ is then calculated from the scattered intensity according to:

$$G(\xi) = \frac{\langle I(t)I(t+\xi) \rangle}{\langle I(t) \rangle^2} \quad (4.10)$$

where, I = intensity; t = time; ξ = delay time

DLS provides information about the fluctuation intensity over time and compares the signal at time t then to a time $t + \xi$.

$G(\xi)$ contains, when modelled as an exponential function, all information required to be entered into the Stokes-Einstein relationship.

$$G(\xi) = B + A \Sigma e^{-2q^2 D \xi}$$

with (4.11)

$$q = \left(4\pi \frac{n}{\lambda_0} \sin \frac{\theta}{2} \right)$$

where, B = baseline at infinite time; A = intercept; q = scattering vector; n = dispersant refractive index; λ_0 = laser wavelength; θ = detection angle

The time when the time autocorrelation function starts to decay indicates the mean particle size and the gradient indicates the polydispersity of the sample (Malvern 2013).

Making Measurements and Analysing the Results After the required time at shear in the Couette device, the crude oil+heptol suspension was rapidly transferred into a glass cuvette (Starna Scientific Ltd.) and placed into the Malvern Zetasizer Nano ZS (Malvern Instruments Ltd). The measured intensity-weighted

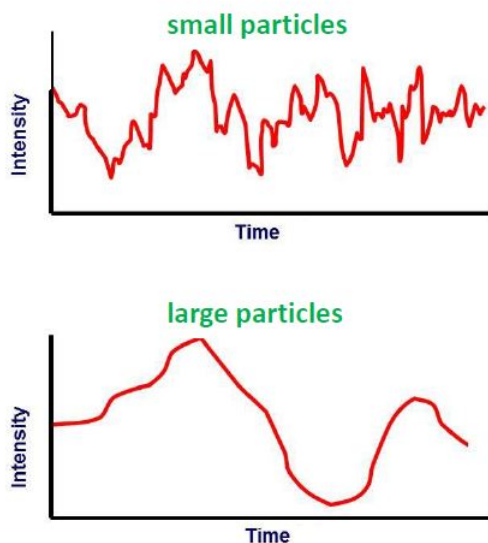


Figure 4.7: Intensity fluctuations due to Brownian motion for different particle sizes.

distribution can be expressed as a volume distribution or a number distribution. For both intensity and volume distributions, the area of the peak for larger aggregates will increase over-proportional with the diameter of the particle as larger particles have both a higher volume (the volume increases with radius³) and scatter much more light than smaller ones, thus dominating the distribution. Hence, both distributions are very sensitive to large particles and dust. As the interest in this experiment, however, lies within detecting the amount of smaller aggregates, which are able to deposit on the capillary wall, the analysis by number distribution was chosen. This type of analysis is best suited for comparative purposes, while still accounting for high intensity aggregates and yet reporting the smallest size measured.

Meeting the Quality Criteria for a Crude Oil Sample It should be mentioned that analysing asphaltene floc size distribution in a crude oil+heptol mixture is not an ideal sample to be measured with DLS as several issues may arise during the measurement:

- Ideally the sample to be measured should be transparent to avoid multi - and backscattering. However, even at low concentrations of asphaltenes and a very small volume of crude oil, this cannot be achieved.
- The refractive index n of the fluid should be different from the the particles ones. Unfortunately, measuring the refractive index of asphaltenes is not conclusive and not straightforward. The asphaltene refractive index can be estimated from dilution experiments, where a long extrapolation is required. Applying that technique, Buckley et al. (1998) has estimated the refractive index of asphaltenes to be about 1.72. Therefore, it was neglected in the measurement which was considered valid as a quantitative data analysis is beyond the scope of this project.
- Due to the complex hydrodynamic nature of asphaltenes in suspension (continuous precipitation, aggregation, floc break up, sedimentation) no stable particle size can be achieved and the sample might be too polydisperse in order to analyse a distribution.
- Some aggregated particle flocs may be too large to be analysed.

Despite the problematic sample, DLS was considered to be a suitable technique as the purpose of this experiment was to show how and if the size varies with different shear rates and mixing times. It was not used to analyse the particle size distribution in detail and quantitatively.

4.2.5 Stochastic Rotation Dynamics (SRD) Simulation

As a comparison to the experimental findings, colloidal asphaltene deposition was modelled in a 2D model, where the asphaltenes are represented as colloidal discs and the solvent as point particles. The colloid interactions are simulated using a

molecular dynamics (MD) method with a defined radius, while the solvent flow field is calculated using stochastic rotation dynamics (Padding and Louis 2006).

To model the asphaltene-asphaltene (a-a) and asphaltenes-wall (a-w) interactions, an interaction potential with variable well depth ε_{a-a} , corresponding to a screened Coulomb potential, was chosen. In terms of the Yukawa functional form, which combines attractive and repulsive interactions, it is expressed as:

$$\phi_{a-a}(\sigma) = \varepsilon_1 \frac{d_1}{\sigma} \exp(\kappa_1(\sigma - d_1)) + \varepsilon_2 \frac{d_2}{\sigma} \exp(\kappa_2(\sigma - d_2)) \quad (4.12)$$

where, ϕ = colloid-colloid interaction; ε_1 and ε_2 = parameters for attraction and repulsion, respectively; σ = distance between colloids; κ^{-1} = Debye screening length; d = colloid diameter

Figure 4.8 shows the graphical representation of the Yukawa potential, where the well depth ε_{a-a} was varied. The well depth then determines the “stickiness” between the colloids: The deeper the well depth, the stronger the forces are keeping the particles “stick” together. By tuning ε_{a-a} over various sets of simulation, the effect of shear rate required to break up the colloids will be studied. The asphaltenes - wall (a-w) interaction will be taken into account by covering the capillary surface with a layer of asphaltenes, meaning the a-a interaction is equal to the a-w interaction. This scenario corresponds with deposition on glass capillary (Padding and Louis 2006); (Boek et al. 2008). A 2D simulation box was chosen with dimensions of $L_x \times L_y = 80 \times 450$ SRD cells, with a number density of 5 SRD particles/cell and the diameter of colloids was set to 3 SRD cells (Boek et al. 2008). Along the direction of flow (y), periodic boundary conditions are applied. The number of asphaltenes was set at a constant value of 700, where 300 of them were fixed to the wall. The remaining 400 free flowing particles were inserted randomly into the SRD fluid. On the contrary, a continuous amount of asphaltenes is supplied in the experiments. The laminar flow will be imposed by applying a body force g_{SRD} to the solvent particles, which

corresponds to a constant pressure drop along the capillary.

$$\begin{aligned} gSRD &= \frac{16Pe}{6\pi r^2 L_x^2} \\ \rho gSRD &= \frac{\Delta p}{\Delta x} \end{aligned} \tag{4.13}$$

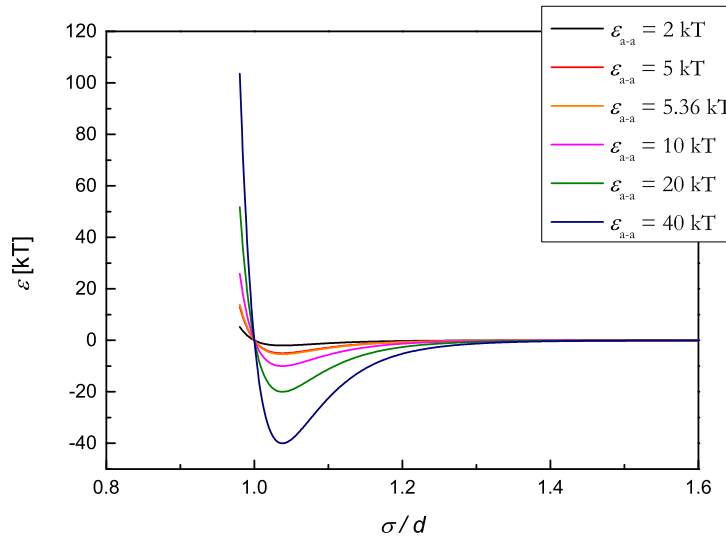


Figure 4.8: Colloid-colloid Yukawa interaction potential. By choosing different parameters for ε_1 and ε_2 , the well depth ε_{a-a} can be varied.

4.3 Results and Discussion

The results are divided into several parts, followed by a summarising discussion at the end. Prior to any deposition experiments, full mixing of the injected fluids and the validity of laminar flow had to be ensured (Section 4.3.1). To assure reproducibility, hence reliability, of the measured pressure drop profiles, several repeat experiments were conducted, shown in Section 4.3.2. Furthermore, the pressure drop

data of some example experiments are related to possible asphaltene deposition on the capillary wall. Next, Section 4.3.3 discusses the effect of a change in heptane fraction in the crude oil+heptol mixture on the deposition rate. Having established a suitable precipitant to diluted crude oil ratio which ensures deposition, the effect of varying the total volumetric flow rate will be described in Section 4.3.4. Additionally, attempts are made to normalise the pressure drop data aiming to reconcile them in terms of the flow rate. The end of each experiments was marked once the pressure has reached a steady state condition and Section 4.3.5 shows optical images of the asphaltene deposits, scanned with CLSM, at steady pressure. In addition, the mass of deposited asphaltenes in the capillary at steady pressure was determined for the flow rates investigated; the results are presented in Section 4.3.6. As it was thought that the asphaltene floc size is an important factor determining deposition, the average floc size was analysed via DLS, where precipitation and aggregation was initiated in the designed Couette reactor in conditions similar to the hydrodynamics in the capillary flow experiments. The relationship between particle size and corresponding capillary flow shear is shown in Section 4.3.7. Depending on the flow rate, a change in deposition kinetics can lead to a different deposition rate; a phenomenon which is discussed in Section 4.3.8. Subsequently, the SRD simulations results are presented, where the fractional deposition was investigated for different Pe numbers, and are then compared to the experimental findings in Section 4.3.9. Additionally, this section addresses the change in uniformity of deposition profile across the capillary length with flow rate. As an interesting relationship between pressure drop, limiting mass of deposits and applied flow rate is revealed in this chapter, a more detailed discussion, outlining several theories governing particle movement within the capillary, is presented in Section 4.3.10. Finally, a homogeneous deposition model is applied to the findings in Section 4.3.11 in order to examine it's validity.

4.3.1 Fluid Mixing before Capillary Transport

To ensure that both co-injected fluid streams mix rapidly after entering the capillary, a static mixer (U-466, Kinesis, U.K.) was used at the inlet. The performance of the mixer was assessed using a de-colourisation reaction, imaged with an optical acquisition system (1-50486, Navitar with single head camera MC2, Photron) as a function of mixing time for different flow rates. The de-colourisation (dark blue $\rightarrow$ colourless) reaction is the oxidation of iodine with sodium thiosulphate in the presence of starch solution (Equation (4.14)). The iodine+starch mixture was co-injected with the thiosulphate solution as described in the experimental set-up section and at the flow rates displayed in Table 5.1. This system (2M iodine + 1M thiosulphate) was chosen as it, due to the high dilution with water, provides a good viscosity match with the crude oil+heptol system. The mixing efficiency was then compared to the mixing with a static mixer.

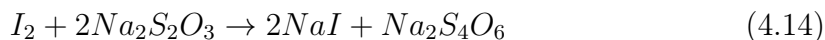


Figure 4.9 shows the comparison between the initial set-up (top) and the enhanced fluid mixing when a static mixer was built in before the fluids enter the capillary (bottom). Three snapshots were taken at the capillary inlet at different times ($t = 5$, 30 and 60 seconds). The first snapshots appear dark which indicates that the iodine solution is evenly distributed throughout the cross-section of the capillary. At $t = 30$ s (second snapshot) the solution is brighter due to mixing with the thiosulphate solution and subsequent de-colourisation. However, for the upper snapshot (no mixer) the lower part of the capillary appears even brighter, which indicates a faster mixing time and hence an uneven mixing process for the entire cross-sectional area.

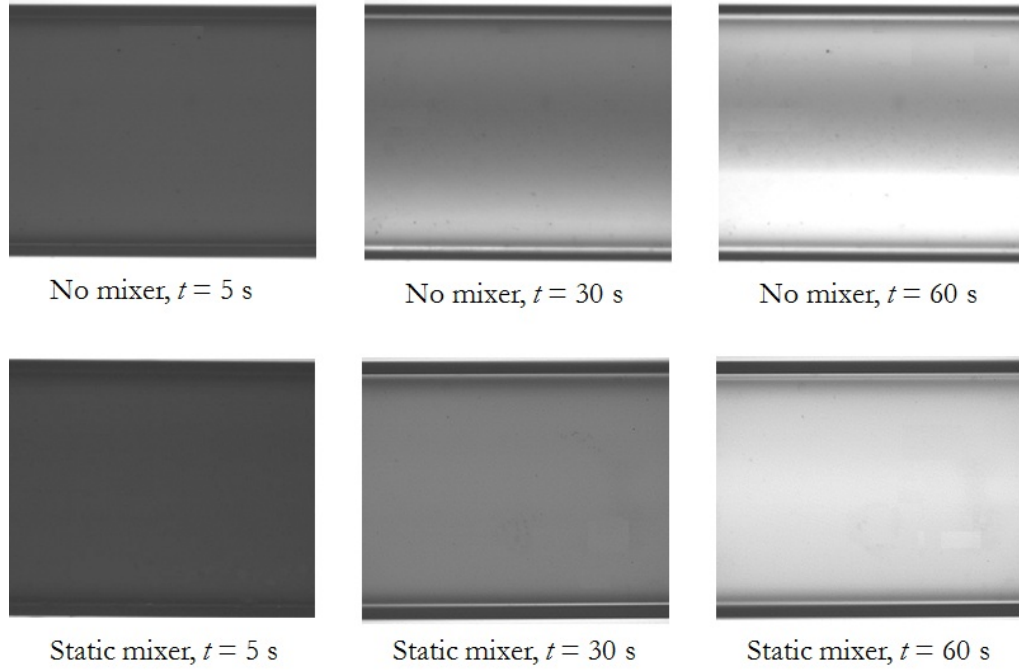


Figure 4.9: Improved mixing with built in static mixer (bottom) when compared to no mixer (top) at $Q_t = 80 \mu\text{L}/\text{min}$.

The effect becomes more pronounced in the last snapshot (no mixer, $t = 60$ s). Full mixing was ensured when the static mixer was used (static mixer, $t = 60$ s).

The Laminar Flow Profile According to the low Re numbers, the fluid flow will exhibit laminar flow through the capillary. The applied volumetric flow rate can be related to the pressure drop Δp through the Hagen-Poiseuille (H.P.) equation (Equation (4.15)). The H.P. equation can be applied to incompressible and Newtonian fluids given the no-slip condition during laminar flow.

$$\Delta p = \frac{128\mu_{\text{heptol}}LQ_t}{\pi d_H^4} \quad (4.15)$$

where, L = capillary length (100 mm); d_H = hydraulic diameter of the capillary (9.09×10^{-5} m)

Figure 4.10 shows the calculated pressure drop Δp for different flow rates. The

viscosity of a heptol solution was measured as described previously and used in Equation (4.15) ($\mu_{\text{heptol}} = (0.898 \pm 0.013) \text{ mPa}\cdot\text{s}$). The pressure drop increases linearly with increasing flow rate. To test the validity of the H.P. equation for the flow in the capillary, the pressure drop was experimentally measured for various volumetric flow rates Q_t . The heptol mixture was co-injected into the capillary as described above (no mixer). The results are shown in Figure 4.10, where for the lower flow rate range the pressure drop increases linearly with flow rate, in agreement with the H.P. equation. The deviations at higher flow rates from the ideal linear behaviour can be attributed due to poor mixing at higher flow rates which may lead to a not fully developed laminar flow. Equation (4.15) was rearranged to calculate the fluid viscosity from the early pressure drop measurements where the linear relationship is applicable.

$$\mu_{\text{heptol}} = \frac{\left(\frac{\Delta p}{Q_t}\right) \pi d_H^4}{128L} \quad (4.16)$$

Applying Equation (4.16), a viscosity for the heptol mixture of $\mu_{\text{heptol}} = 0.897 \text{ mPa}\cdot\text{s}$ was calculated. This is within the standard deviation of the experimental value, thus showing the reliability of the data points obtained in the low pressure range. To ensure a uniform deposition across the capillary, full mixing and to account for the deviations in the pressure drop at higher flow rate, the pressure drop response to changing flow rate was measured when the Y-connector was changed for a static mixer. The pressure drop responds linearly to the change in flow rate, however with a steeper slope when compared to the experiments without mixer, as the mixer gives an additional pressure drop not accounted for in the HP equation. Several deposition experiments were carried out and no effect on the pressure drop due to eventual deposition in the mixer was observed.

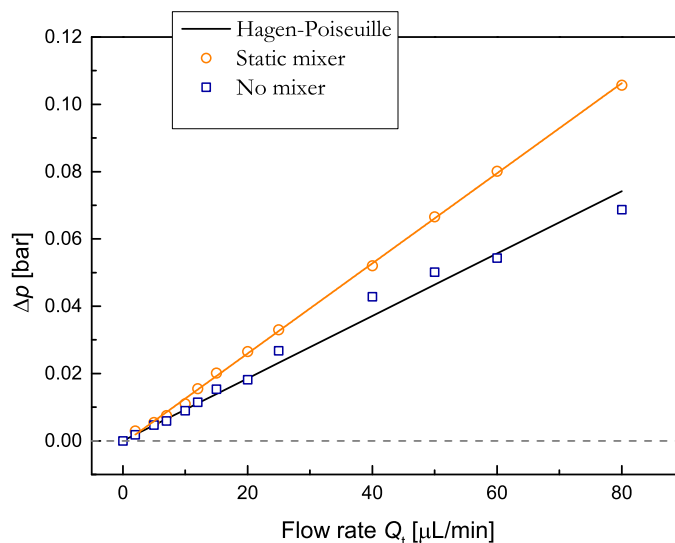


Figure 4.10: Comparison of the linear relationship between pressure drop *vs.* flow rate of heptol calculated from the Hagen-Poiseuille equation and by using the static mixer in the empty glass capillary. The displayed pressure drop was measured by flowing a heptol solution through the capillary.

4.3.2 Reproducibility of the Experimental Data

Prior to analysis of the effect of any flow parameters on the deposition behaviour, the reproducibility and hence the reliability of the pressure drop profiles had to be ensured. This sections also discusses the change in transient pressure drop caused by deposition on the walls. Figure 4.11 shows an example for a pressure drop history at a total volumetric flow rate $Q_t = 10 \mu\text{L/min}$ and a heptane to oil volume/volume ratio $R = 3$ to 1.

Three repeat experiments were carried out at ambient conditions. The experiments were reproducible within an error margin of 13% in pressure drop, which suggests confident data for subsequent runs. For all experiments, a small induction period was observed, followed by an increase in pressure drop. This indicates that asphaltenes do not deposit immediately after precipitating from the crude oil within

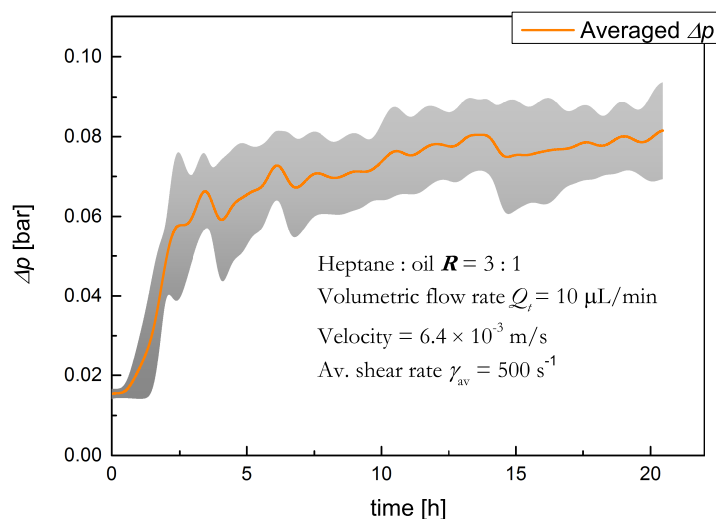


Figure 4.11: Averaged pressure drop Δp *vs.* time profile at a constant flow rate of $10 \mu\text{L}/\text{min}$ and a heptane : oil ratio $R = 3 : 1$. The grey shaded area shows the standard deviation from three repeat experiments.

the sensitivity of the pressure transducer, suggesting that the asphaltene-wall interaction is weaker than the asphaltene-asphaltene interaction. The increasing pressure drop corresponds to a continuous deposition of asphaltenes on the capillary wall. At later times, the slope of the pressure drop decreases, indicating a lower deposition rate. The pressure eventually levels off, suggesting that less asphaltenes deposit on the existing deposit layer.

4.3.3 Effect of Precipitant Fraction

The first parameter to be studied in the following section is the change in heptane fraction which was co-injected into the capillary. Figure 4.12 shows the pressure drop history for three example experiments at a constant volumetric flow rate $Q_t = 10 \mu\text{L}/\text{min}$ at different heptane : oil+toluene ratios R .

No significant change in the pressure drop was observed for the experiment with

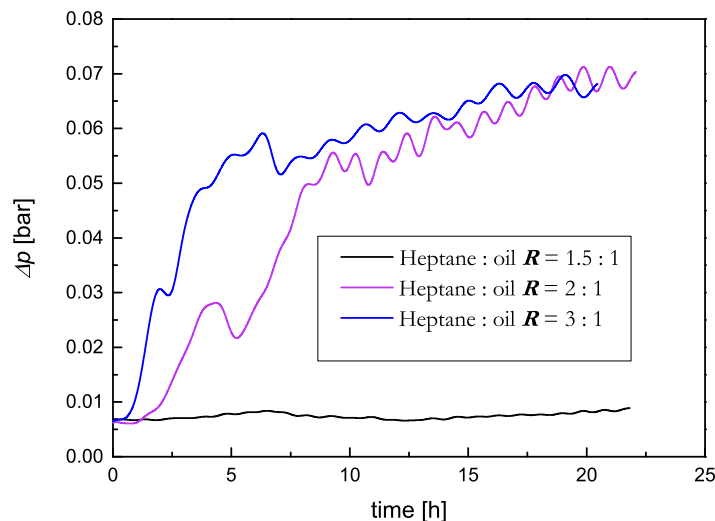


Figure 4.12: Pressure drop Δp vs. time profile for a constant flow rate of $10 \mu\text{L}/\text{min}$ at different heptane fractions ($R = 1.5, 2$ and 3).

the lowest precipitant to oil+solvent ratio ($R = 1.5$), indicating that no asphaltenes deposited within the pressure and time range measured. In Chapter 3 and Seifried et al. (2013b), the precipitation onset for the Zuata crude oil was determined to be $\delta_{\text{onset}} = 16.45 \text{ MPa}^{0.5}$, whereas the mixture at $R = 1.5$ has a mixture solubility parameter $\delta_{\text{mixture}} = 16.39 \text{ MPa}^{0.5}$. Seifried et al. (2013b) discussed that in this regime asphaltenes precipitate from crude oil and that the kinetics of the aggregation follow a crossover behaviour between diffusion-limited aggregation (DLA) and reaction-limited aggregation (RLA). Although the mixture solubility parameter is lower than the precipitation onset solubility parameter and the precipitant/solvent ratio exceeds the minimum threshold required for precipitation, asphaltenes did not deposit on the capillary walls within the sensitivity of the pressure transducer.

In Seifried et al. (2013b), the mean aggregate size was analysed using images taken with CLSM. The mean floc sizes presented in this paragraph may vary from the DLS measurements presented further below as DLS size analysis does not take

sedimented particles into account. The average diameter at the precipitation onset point after a short period of time (similar to the residence time of the flow rate $Q_t = 5 \mu\text{L}/\text{min}$) was found to be around $1.5 \mu\text{m}$. Increasing the precipitant fraction in the mixture leads to a higher precipitation rate and a higher average asphaltene aggregate diameter ($150 \mu\text{m}$ for $R = 3$ at $\delta_{\text{mixture}} = 15.94 \text{ MPa}^{0.5}$). With increasing precipitation rate, the overall polydispersity increases as well with aggregates in the size range of 3 to $180 \mu\text{m}$. The experiments to determine the mean aggregate size were carried out in a batch reactor, due to the difficulty in measuring the size distribution in capillary flow. Because of the different hydrodynamics, smaller flocs are to be expected in the capillary flow experiments. The smaller aggregates diffuse to the wall and deposit, whereas the bigger flocs remain in the bulk flow (Eskin et al. 2011). The rate of asphaltene aggregates supplied seems to be the determining factor in the deposition process.

4.3.4 Effect of Volumetric Flow Rate

Considering that a higher fraction of precipitant leads to a higher pressure drop and possibly more deposition, a ratio of $R = 3$ was chosen for the subsequent experiments. In the following section the effect of change in the total volumetric flow rate is analysed. The measured pressure drop data are then normalised with the aim to produce a master curve.

Figure 4.13 shows the effect of volumetric flow rate on the deposition behaviour. The flow rate was varied from $2 \mu\text{L}/\text{min}$ to $5 \mu\text{L}/\text{min}$ and to $10 \mu\text{L}/\text{min}$ at a constant heptane : oil ratio $R = 3$. In all three experiments, the deposition follows a similar trend: A short induction time is followed by an increase in pressure drop, indicating an increase in deposition rate. Subsequently, the deposition process slows down until the pressure levels off indicating that deposition is limited. In all three experiments, erosion and entrainment cycles are observed.

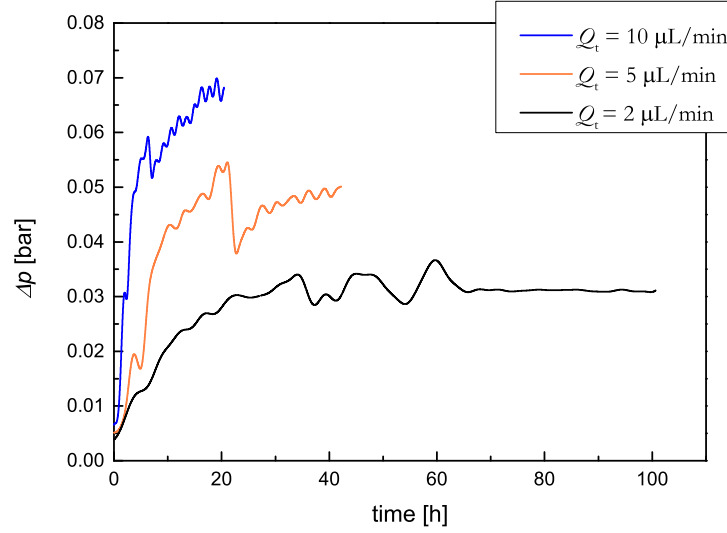


Figure 4.13: Pressure drop Δp *vs.* time profile for a constant ratio $R = 3$ at three different volumetric flow rates. The same volume of fluid was displaced through the capillary at all flow rates.

Steady Pressure The steady pressure due to a dynamic equilibrium between entrainment and deposition can further be explained by looking at the different forces acting on a particle attached to a surface: The particle experiences adhesive forces predominantly by gravity (F_G) and attractive v.d.W. forces ($F_{v.d.W.}$), which are not affected by the flow. For small particles it is, however, valid to neglect gravity. The adhesive contribution F_A is thus given by:

$$F_{v.d.W.} = \frac{H a_p}{12 z_0^2} \quad (4.17)$$

where, H = Hamaker constant; z_0^2 = distance of minimum approach between particle and surface (assumed to be constant)

Any flow will exert a hydrodynamic force on the particle and if they become large enough to overcome the adhesion forces, the flocs will be detached from the surface

and entrained in the flow. They can be removed by drag forces F_D and also shear-induced lift forces F_L are acting on the particle in the opposite direction of the attractive v.d.W. forces. However, the drag force is significantly larger than the lift force, particularly for particles deposited on a lumpy wall. Also, surface friction F_F acting opposite of F_D has no significant effect on the attached floc (Eskin et al. 2011). In laminar flow for micron sized particles the drag force is defined as (Zoetewij et al. 2009):

$$F_D = 1.7 \times 3\pi\mu a_p v \quad (4.18)$$

To derive the force balance it is sufficient to consider F_A and F_D only. The criterion for particle removal is therefore:

$$\begin{aligned} F_D &\geq F_F(F_{v.d.W.} + F_G - F_L) \\ \therefore F_D &\geq F_{v.d.W.} \end{aligned} \quad (4.19)$$

At steady state the dynamic equilibrium can be mathematically expressed as:

$$F_H = F_A \quad (4.20)$$

where, F_H = hydrodynamic force required for entrainment and detachment, here: $F_H = F_D$; F_A = adhesive force, here: $F_A = F_{v.d.W.}$.

Normalising the Pressure Drop Data A notable difference between the three flow rates is the initial deposition behaviour with an increase in deposition rate with higher flow rate. This suggests that with higher flow rate asphaltenes deposit faster at earlier times. To further investigate the deposition kinetics, more flow rates

were studied and normalised by the injected capillary volumes (CV) (Figure 4.14). By normalising the flow rate by CV, the initial gradients look more similar, suggesting that the early deposition behaviour is independent of the injected volume. The early deposition depends mostly on the flux of particles through the capillary per unit time.

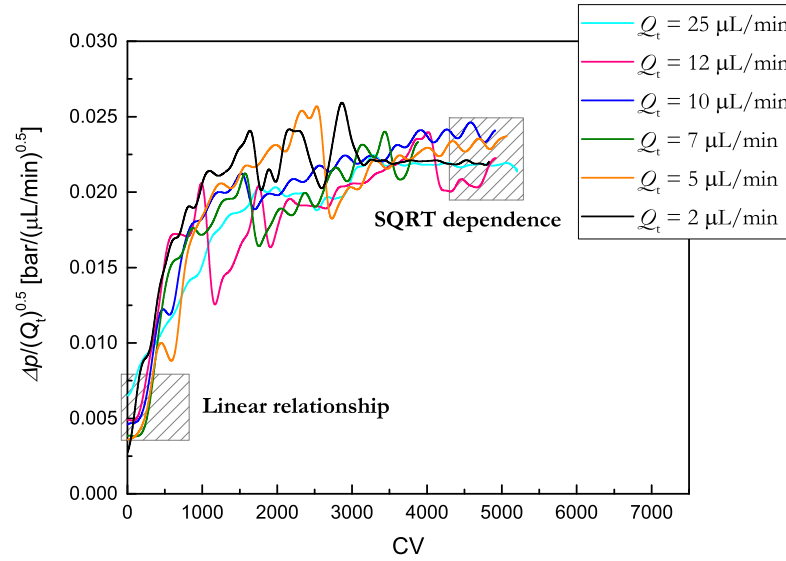


Figure 4.14: Normalised pressure drop profile ($\Delta p/(Q_t)^{0.5}$) for a constant ratio $R = 3$ at different volumetric flow rates.

In agreement with Hagen-Poiseuille, the pressure drop shows a linear dependence of the flow rate in the empty capillary prior to any asphaltene deposition. However, all pressure drop profiles collapse on a master curve, when they were normalised by the square-root (SQRT) of the flow rate ($(Q_t)^{0.5}$), showing a clear deviation from the linear relationship (Figure 4.14).

Subsequent analysis of the asphaltene deposition is carried out at steady pressure, as no information are available about the transient pressure drop data. Figure 4.15 shows the pressure drop at steady pressure at each flow rate on a log/log graph, showing a linear relationship with an exponent of 0.46, which is approximated to a

square-root behaviour in further analysis.

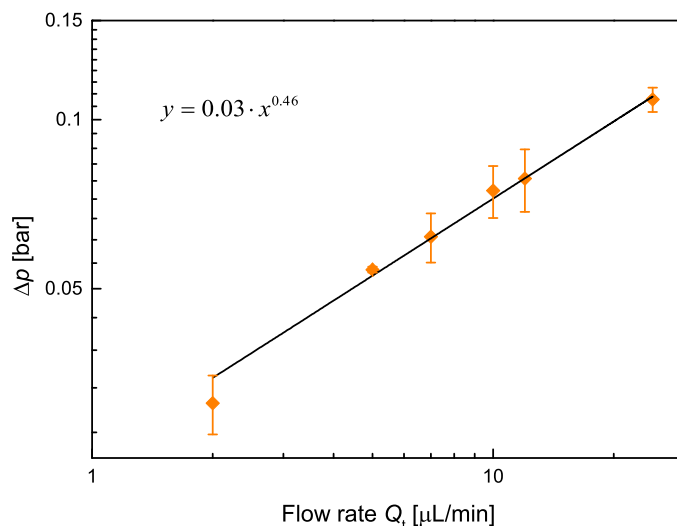


Figure 4.15: Increase in pressure drop at steady pressure with the square-root of the volumetric flow rate. The error bars were calculated from repetitions at each flow rate.

4.3.5 Imaging the Asphaltene Deposits

The advantage of using a glass capillary is that the asphaltene deposits can be observed visually, which provides a further insight into the deposition behaviour at steady pressure.

Figure 4.16 illustrates the images taken with CLSM at the steady pressure condition at the flow rates $Q_t = 2, 5$ and $10 \mu\text{L/min}$. The images show the asphaltenes, as black spots, adsorbed on the capillary wall. With increasing flow rate, more asphaltene deposits appear at the capillary inlet. At the capillary outlet, however, no significant change can be observed between the three flow rates investigated. The increase in appearance of black dots with increasing flow rate also seems to be in agreement with the pressure drop data, where the increase in final Δp can be

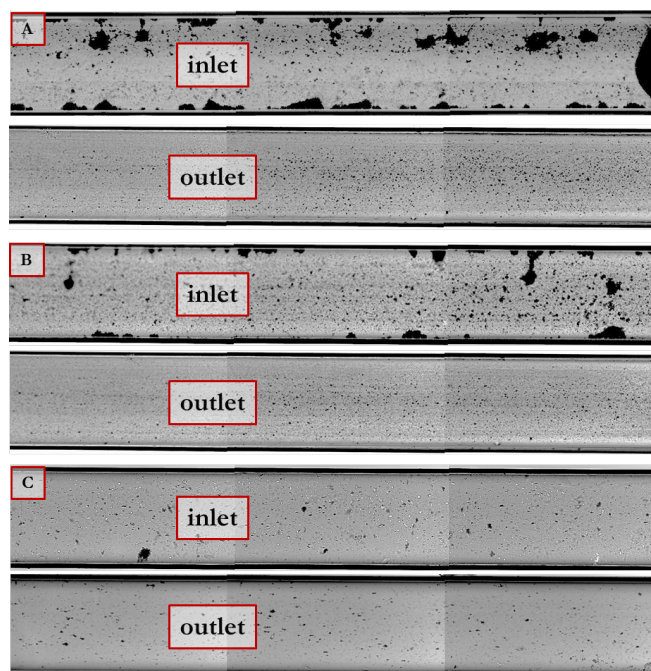


Figure 4.16: Different sections of the capillary imaged with CLSM at various flow rates at $R = 3$. **A:** $Q_t = 10 \mu\text{L}/\text{min}$; **B:** $Q_t = 5 \mu\text{L}/\text{min}$; **C:** $Q_t = 2 \mu\text{L}/\text{min}$. A section of 1 cm away from the capillary inlet and 5 mm from the capillary outlet was scanned after the experiment, which each image corresponding to a capillary length of 3.6 mm in the direction of flow (from right to left). All images show the top view of the capillary (Seifried et al. 2013a).

correlated to more deposits in the capillary.

4.3.6 The Mass of Asphaltene Deposits

To confirm the observations made above that the amount of deposited asphaltenes at steady pressure increases with flow rate, the mass of deposits was determined directly by weighing the capillary before and after the experiments on a high precision balance. Before weighing, the capillary was dried in an oven to ensure that the remaining solvent had evaporated.

Table 4.4 summarises the average mass for three independent measurements from three different deposition runs including their standard deviation. The results are

graphically represented in Figure 4.17. Interestingly, the final mass of deposited asphaltenes increases with the square-root of the flow rate, which is a similar behaviour observed for the steady pressure drop *vs.* flow rate relationship.

Table 4.4: Measured mass of deposited asphaltenes in the capillary at different volumetric flow rates including the deviation from three repetitions.

Flow rate Q_t [$\mu\text{L}/\text{min}$]	Mass $\times 10^3$ [g]
2	0.17 ± 0.014
5	0.25 ± 0.014
7	0.29 ± 0.022
10	0.35 ± 0.013
12	0.37 ± 0.023
25	0.54 ± 0.034
60	0.69 ± 0.081
80	0.88 ± 0.088

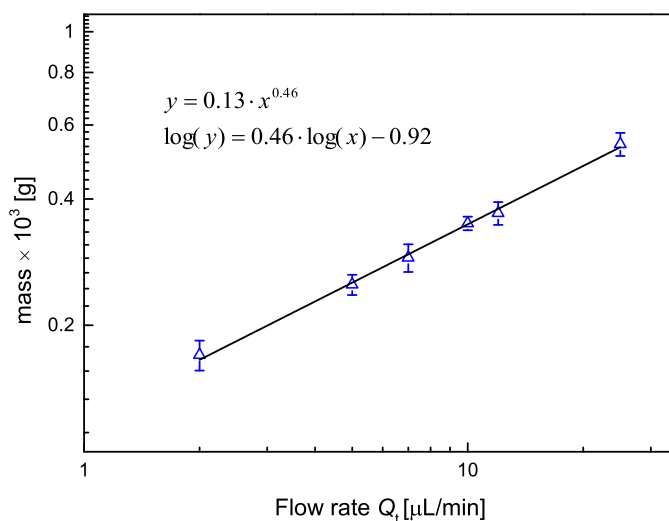


Figure 4.17: Increase in mass of deposited asphaltenes in the capillary with volumetric flow rate. The data are plotted on a log/log scale, showing that the mass increases linearly with the square-root of the volumetric flow rate. The values for the flow rates of 60 and 80 $\mu\text{L}/\text{min}$ are discussed in a later section.

4.3.7 Measuring the Floc Size and Size Distribution

The force balance established above has shown a dependence of deposition on particle size. A logical step in understanding the relationship between mass and flow rate is thus to gain a further insight into the change in particle size with flow rate and residence time.

In this work, the change in mean aggregate size was measured via DLS, where precipitation and aggregation were induced by mixing the diluted crude oil and heptane in a Couette mixer. To simulate the hydrodynamic conditions in the capillary flow experiments, the stirrer speed was adjusted according to the applied shear rate and the stirring time was set to match the residence time at the corresponding volumetric flow rate. Table 4.5 shows the experimental conditions in the Couette experiments. Each experiment was prepared and analysed three times to ensure reproducibility. Visible examination after the experiment showed that no deposition occurred on the mixer wall, therefore the measured floc size represents the floc size in the bulk at the capillary outlet prior to any deposition and after experiencing shear.

Table 4.5: Applied stirrer speed and reaction time in the Couette mixer to simulate the capillary flow experiments. The last column shows the measured mean floc size.

Experiment	Stirrer speed rpm [min ⁻¹]	Reaction time [s]	Mean floc diameter [μm]
#1	50.02	30	4.13 ± 0.93
#2	70.03	21	3.54 ± 1.23
#3	100.04	15	0.63 ± 0.43
#4	120.05	13	0.59 ± 0.23
#5	250.10	6	0.39 ± 0.22

It should be noted, that the stirrer time is purely the time of the reactants being in the Couette mixer. The time used for transferring the sample into the glass cuvette

and subsequent data analysis was assumed to be constant, even though further aggregation, floc break up and sedimentation might have still occurred. Figure 4.18 shows the particle size distribution by number obtained from DLS analysis for one of the three runs (#1-#5), where the measured floc diameter d and their percentage occurrence in the sample is shown. The sample from experiments #1-#3 only contain particles with one size within the size range measured. Experiments #4 and #5 show a bimodal distribution, where 3% of the particles are larger than $4.5\ \mu\text{m}$ (experiment #4) and 5.2% are particles larger than $4.3\ \mu\text{m}$ for experiment #5. Overall the mean aggregate size decreases with increasing shear rate and shorter reaction time. This trend is highlighted in Figure 4.19, where the floc size is plotted against the corresponding flow rate in the capillary flow experiments, as shown in Table 4.3. The error bars in the vertical direction indicate the deviation from three independent measurements.

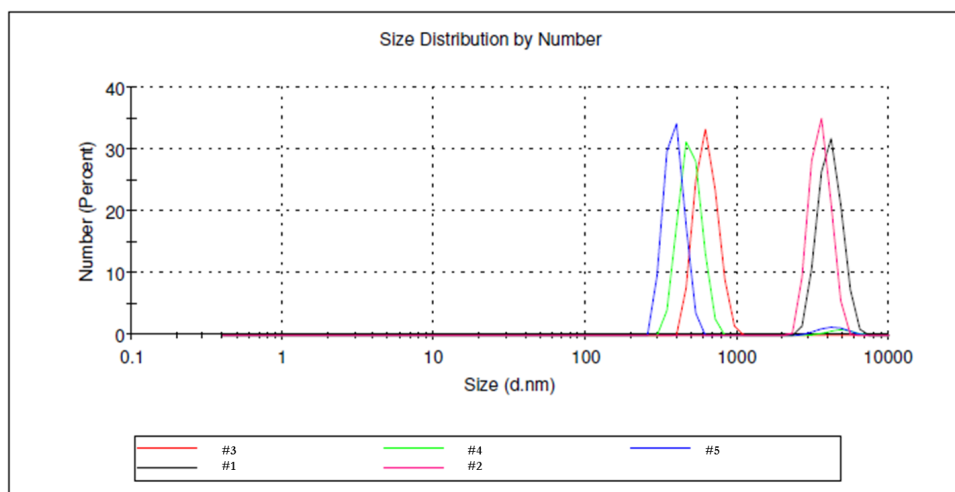


Figure 4.18: Particle size distribution by number obtained from DLS for one set of experiments.

After precipitation, asphaltenes tend to aggregate in the bulk flow. Higher shear rate will lead to a higher collision frequency among the particles, thus leading to

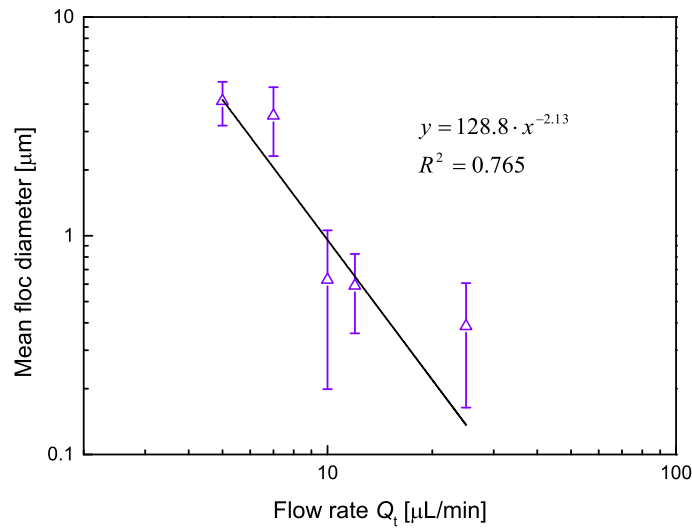


Figure 4.19: Change in floc diameter, measured with DLS, with volumetric flow rate applied in the capillary flow experiments.

a faster aggregation rate, resulting in a counter effect: The higher hydrodynamic stress due to higher shear acting on these flocs causes them to break up again. The aggregates are then present as loose flocs in the bulk and the larger an aggregates becomes, the more susceptible it is to subsequent break up. As the mean floc size decreases with increasing shear rate, suggest that the shear induced fragmentation of flocs dominates over the collision rate. These results are similar to the ones reported by Rahmani et al. (2003), where the change in asphaltene floc size was monitored through image analysis. The authors found a decreasing steady state floc size with increasing shear.

4.3.8 Shear-Limited *vs.* Diffusion-Controlled Deposition

In the literature (Section 2.4.3), two different main deposition regimes were identified by Nabzar and Aguilera (2008): At low shear rates the deposition kinetics follow the colloidal laws for **diffusion-controlled** deposition and beyond a certain critical

shear rate the regime is called **shear-limited** deposition.

Additional experiments beyond the previously studied flow rates (2 - 25 $\mu\text{L}/\text{min}$) were conducted for $Q_t = 60$ and 80 $\mu\text{L}/\text{min}$ to investigate the asphaltene deposition behaviour. In agreement with Figure 4.10, the relationship between flow rate and pressure drop for the empty capillary (before deposition) is linear. Figure 4.20a shows that for the entire range of flow rates investigated the final pressure drop depends on the square-root of the applied flow rate. The pressure drop for $Q_t = 80$ $\mu\text{L}/\text{min}$ should be treated carefully, as the pressure may not have reached steady state yet.

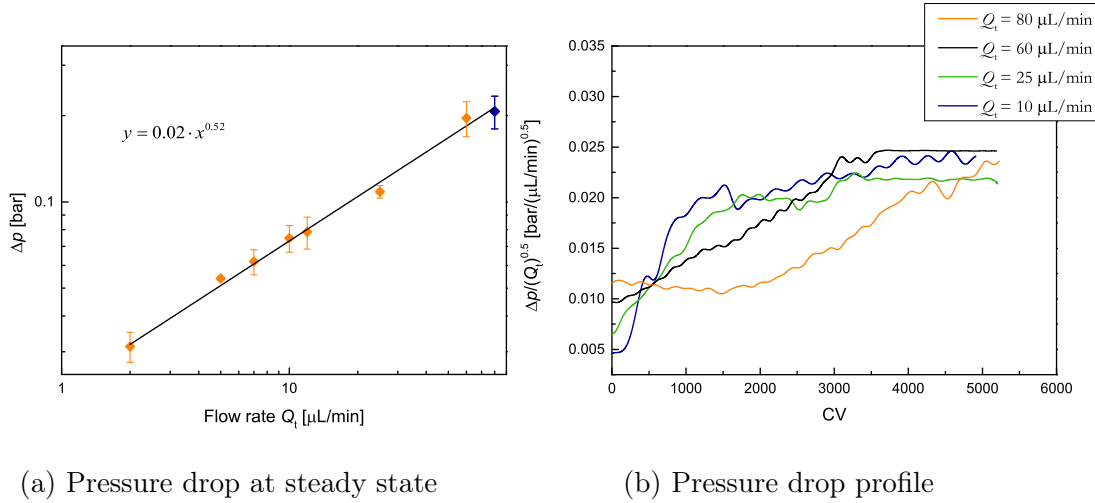


Figure 4.20: Normalised pressure drop profiles at four different flow rates (10 - 80 $\mu\text{L}/\text{min}$). The square-root dependence is further highlighted on a log/log graph for all flow rates studied. The pressure drop at $Q_t = 80$ $\mu\text{L}/\text{min}$ is shown in blue as a reminder to treat this value carefully.

Simultaneously, the capillary inlet was imaged *in-situ* for the flow rates $Q_t = 10$ and 80 $\mu\text{L}/\text{min}$, where a snapshot was taken at selected CV (Figure 4.21). The number of adsorbed black spots increases with more fluid volumes injected, however, the steady state condition in terms of amount of deposits is reached earlier at the lower flow rate. This is in agreement with the pressure drop data, shown in Figure 4.20b,

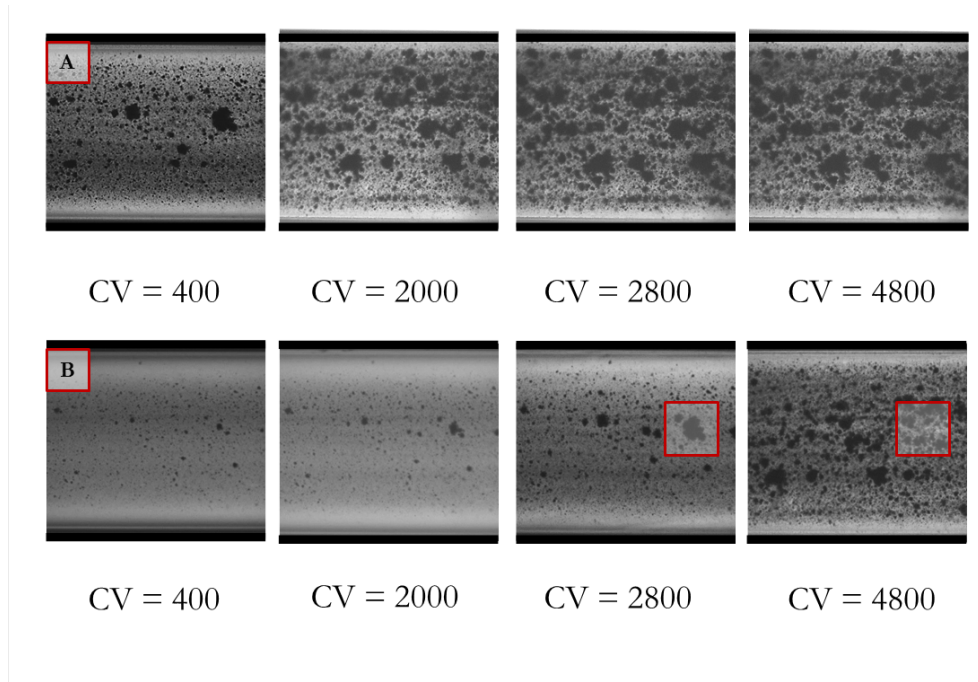


Figure 4.21: Snapshots of asphaltene deposition at two different flow rates for selected injected CV. **A:** $Q_t = 10 \mu\text{L}/\text{min}$; **B:** $Q_t = 80 \mu\text{L}/\text{min}$. Each image was taken at 1 cm away from the capillary inlet with a length of 1.3 mm in the direction of flow (from left to right). The red box highlights an asphaltene floc which became entrained in between the two snapshots due to shear.

and the theory by Nabzar and Aguilera (2008) stating that above a critical shear rate, the deposition kinetics are slowed down which is indicated by a lower deposition rate. Above this threshold the deposition regime changes from diffusion-controlled deposition into the shear-limited regime, with the pressure drop data suggesting that the shear-limited regime has been reached at a flow rate between 25 and 60 $\mu\text{L}/\text{min}$. Due to higher shear in this regime, entrainment of asphaltenes in the flow becomes more likely.

4.3.9 Stochastic Rotation Dynamics (SRD) Simulation

Similar to Boek et al. (2008) and Boek et al. (2010), SRD computer simulations were carried out to support the above findings. Firstly, the simulation results are presented, which are then compared to the experimental results.

Simulation Results EFFECT OF PECLET NUMBER: The first set of simulation compares different Pe numbers calculated from the body forces gSRD at a constant well depth of $\varepsilon_{a-a} = 5$ kT (Figure 4.22). For each Pe , 10 simulations were performed and then averaged over the number of runs. An example of the input file for $Pe = 10$ and $\varepsilon_{a-a} = 5$ kT is shown in Section C.1. Figure 4.22 shows the results for various Pe where a channel width of $nx = 80$ SRD cells was considered. The fraction of deposited particles as a function of SRD time steps is displayed and shows that with increasing Pe , corresponding to increasing flow rate, the fraction of deposited particles decreases at steady state. For lower flow rates ($Pe = 1, 2, 5$ and 10), almost all of the free flowing particles deposit on the capillary wall, whereas a drastic drop is observed for the the higher flow rates: The fraction of deposited particles decreases to almost 0.5 for $Pe = 50$.

In Figure 4.23, the steady state behaviour through simulation snapshots for $Pe = 1$ and $Pe = 50$ is observed. For $Pe = 1$, the deposition shows significant irregularities, the particles seem to deposit in heterogeneous aggregates across the length of the capillary. For $Pe = 50$ less colloids deposited at steady state, the remaining ones are flowing as free flocs through the capillary. The deposits, however, are more evenly and homogeneously distributed on the capillary wall. The increased flow rate may have smoothen out the inhomogeneity.

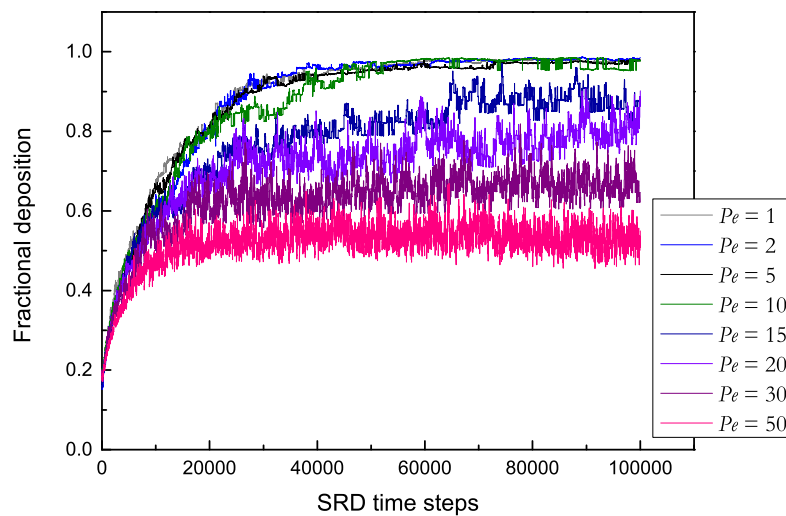


Figure 4.22: Fraction of deposited particles as a function of SRD time steps for $\varepsilon_{a-a} = 5$ kT and $nx = 80$.

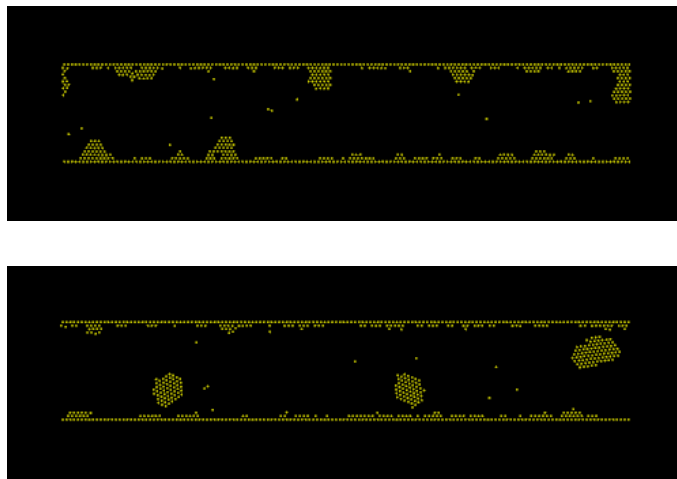


Figure 4.23: Simulation snapshot for $Pe = 1$ (top) and $Pe = 50$ (bottom) at $\varepsilon_{a-a} = 5$ kT.

EFFECT OF WELL DEPTH: In the next simulation set, the effect of changing well depth ε_{a-a} (“stickiness” between the particles) for a constant $Pe = 5$ was studied. With a deeper potential depth the “stickiness” of the particles increases which results in a higher deposition rate (Figure 4.24). No significant fraction of particles deposited for a lower well depth, as here the colloidal thermodynamic forces are not sufficient enough to lead to deposition. Figure 4.25 shows the corresponding simulation snapshots at steady state. For a well depth of $\varepsilon_{a-a} = 2$ kT the colloids neither seem to aggregate to flocs nor deposit on the wall, which is in agreement with Figure 4.24. The “stickier” the particles become, the more flocs are formed which deposit in heterogeneous clumps on the capillary wall. The deposition appears to be more dominant the deeper the well depth is.

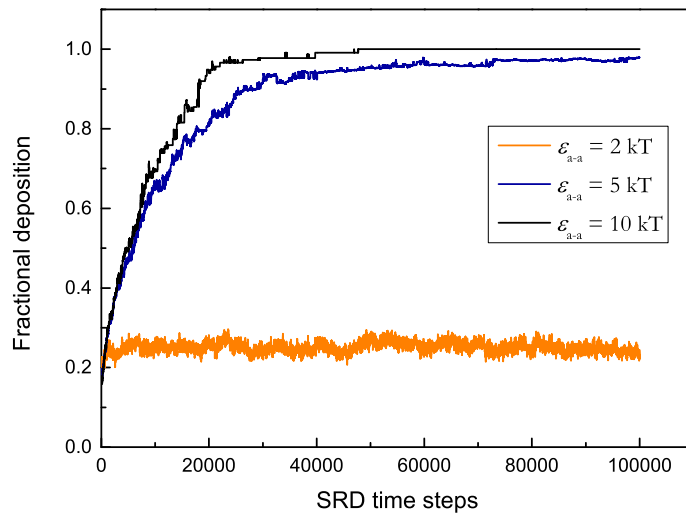


Figure 4.24: Fraction of deposited particles for variable well depth ε_{a-a} and $Pe = 5$.

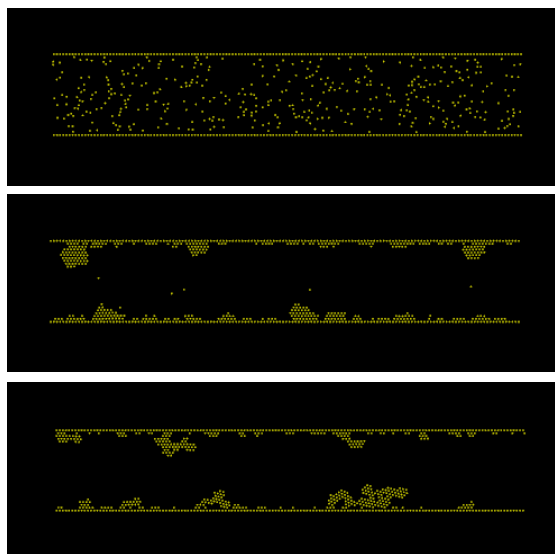
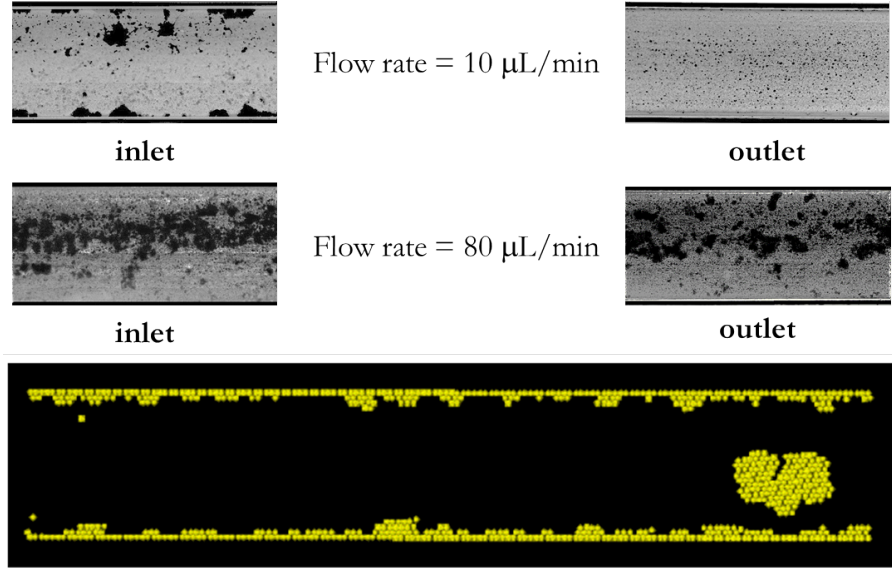


Figure 4.25: Simulation snapshot for $Pe = 5$ at various well depths ε_{a-a} . $\varepsilon_{a-a} = 2$ kT (top); $\varepsilon_{a-a} = 5$ kT (middle); $\varepsilon_{a-a} = 10$ kT (bottom).

Comparison to Experiments Figure 4.22 shows that the fraction of deposited colloids decreases with increasing Pe (flow rate) for $Pe = 10 - 30$, this indicates that the range of Pe chosen in the simulations lies within the shear-limited regime. This is in agreement with Figure 4.20b, where the asphaltene deposition rate decreases with increasing volumetric flow rate. Figure 4.26 compares a simulation snapshot for $Pe = 30$ at $\varepsilon_{a-a} = 5$ kT with optical images taken at steady pressure ($Q_t = 10$ and $80 \mu\text{L}/\text{min}$). From both simulation and experimental results, it can be concluded that deposition occurring in the shear-limited regime results in a more uniform deposition profile. It should be noted though, that the seemingly low Pe numbers in the simulation cannot be extrapolated to the experimental Pe , which are in the range of $10^6 - 10^7$, because the well depth in the experiments might probably be higher. Additionally, applying periodic boundary conditions does not entirely represent the experimental conditions. A continuous supply of precipitated asphaltenes is not guaranteed and the size of the flowing flocs in the bottom snapshot

of Figure 4.23 might be overestimated as they continuously keep growing throughout the simulation.



Simulation snapshot $Pe = 30$ at steady state

Figure 4.26: Comparison between optical images of asphaltene deposits and a simulation snapshot. The capillary was imaged at steady pressure at two different flow rates: $Q_t = 10 \mu\text{L}/\text{min}$ (top) and $Q_t = 80 \mu\text{L}/\text{min}$ (middle). Below a simulation snapshot at steady state is shown for $Pe = 30$.

4.3.10 The Relationship between Pressure Drop, Mass and Flow Rate

In the previous sections the results from several experiments and simulations have been described. Below are all main findings listed which are discussed and analysed further in the following section:

- With increasing flow rate the pressure drop increases more steeply in time, indicating more deposition with higher shear. Eventually, the pressure drop

reaches steady state with a dependence on the square-root of the applied flow rate.

- Higher pressure drop indeed corresponds to more deposits, assessed through imaging and mass measurements, in a way that the mass depends linear on the pressure drop and on the square-root of the flow rate.
- The mean particle size decreases with higher shear, giving an indication that the deposition shows a sensitive response to the particle size.
- Establishing a force balance confirmed the particle size dependence, concluding that a smaller particle experiences smaller hydrodynamic forces, hence a higher sticking probability and finally resulting in more deposition at higher flow rate.
- Beyond a critical shear rate, the deposition rate slows down with a more homogeneous deposition profile across the length of the capillary. The relationship between mass and the square-root of the flow rate remains unchanged regardless of the deposition regime.

The Change of Mass and Floc Diameter with Flow Rate The relationship between the particle diameter and the corresponding flow rate (Figure 4.19), which is considered to be valid for $R = 3$ and ambient conditions, was fitted with the following power law equation:

$$d = 128.8 \times Q_t^{-2.13} \quad (4.21)$$

Rearranging the fit to Q_t shows a square-root relationship between the flow rate and

the floc diameter:

$$\begin{aligned} Q_t &= \frac{c}{d^{0.47}} \\ \therefore Q_t &\propto \frac{1}{\sqrt{d}} \end{aligned} \quad (4.22)$$

where, c = constant

As seen in Figure 4.17, the limiting mass depends on the square-root of the flow rate:

$$m \propto \sqrt{Q_t} \quad (4.23)$$

Combining these two relationships, shows that the mass of deposited asphaltenes correlates to the particle diameter as shown in Equation (4.24). It should be noted that this expression might not entirely represent the relationship between the limiting mass at steady pressure and the diameter, as the floc size measured corresponds to the particle size at the capillary outlet after shear. This empirical relationship is described at:

$$m \propto \left(\frac{1}{d}\right)^{0.25} \quad (4.24)$$

In summary it can be said that the higher shear causes a net decrease in particle size due to floc break up, a process which is dominating here over collision. As the diffusion coefficient is inversely proportional to the particle length scale (Equation (4.3)), smaller flocs experience a higher diffusion rate to the wall, thus leading to more deposition (Figure 4.17). This concept may be supported by Vargas and Chapman (2010) and Hoepfner et al. (2013), who stated that only sub-micron particles are able to deposit.

The values for the measured mass in Table 4.4 are graphically illustrated in Figure 4.27, where the blue triangles show the experimentally determined mass. As there is a significant gap between the flow rates investigated, the fit displayed in Figure 4.17 was used to predict the mass for $Q_t = 60$ and $80 \mu\text{L}/\text{min}$ (orange triangles). Correlating the mass for these flow rates and comparing it to the experimental values, shows that the relationship between the mass and the particle diameter is still valid even at higher flow rates when being in the shear-limited regime.

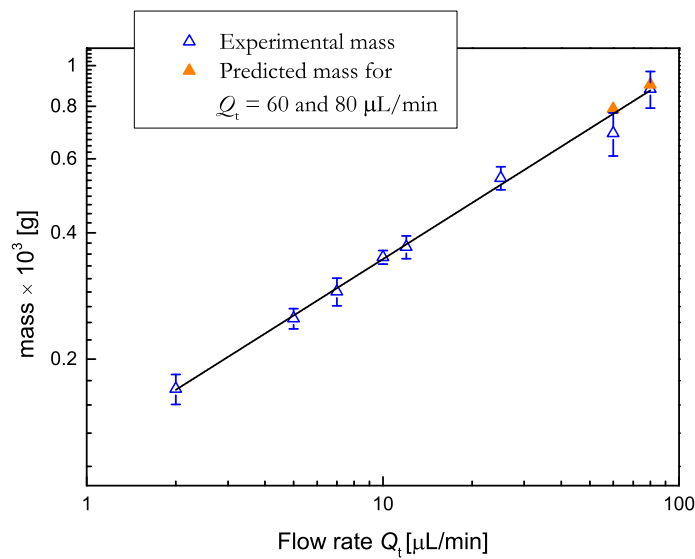


Figure 4.27: Experimentally determined mass at all flow rates (blue triangles) compared to a correlated mass for the two flow rates in the shear-limited regime (orange triangles). The solid line is a fit to all experimental data.

The Pressure Drop and Flow Rate Relationship Interestingly, similar to the mass-flow rate relationship, the pressure drop at steady state increases with the square-root of the flow rate (Figure 4.28). This seems counter intuitive at first as it means that the conductance of the capillary increases as the mass of deposited asphaltenes increases. Additionally, the linear relationship between pressure drop

and flow rate in the empty capillary in terms of the H.P. relationship is also displayed in Figure 4.28, emphasising this intriguing behaviour. Possible reasons are discussed hereinafter with the paragraph being divided into three parts **A-C**.

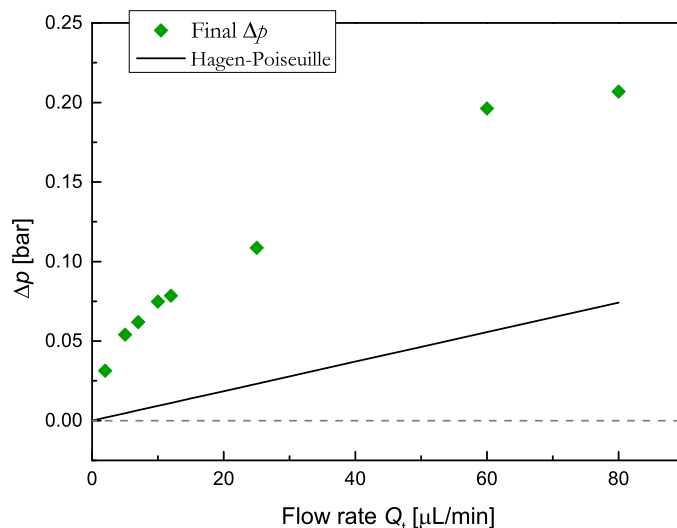


Figure 4.28: Square-root relationship between Δp and flow rate compared to the ideal linear behaviour in an empty capillary.

(A:) THE DISRUPTION IN LAMINAR FLOW PROFILE: The asphaltene deposits change the smooth structure of the empty capillary into a lumpy wall, probably affecting the hydrodynamics of the fluid flow and simultaneously changing the diameter of the capillary. Both experiments and simulations at higher flow rate and higher Pe respectively, have shown that the deposition occurs more homogeneously along the capillary with free clusters travelling down the capillary. It can be assumed that these clusters might generate disruptions in the solvent flow profile, resulting in a non-fully developed Poiseuille profile (Figure 4.29). Over large time scale the flow profile is unaffected by these clusters, however, by averaging the flow field over a short time scale at $Pe = 30$ a deviation in the laminar flow field can be observed, which might be indicative of possible local plug flow occurring (Boek et al. 2016).

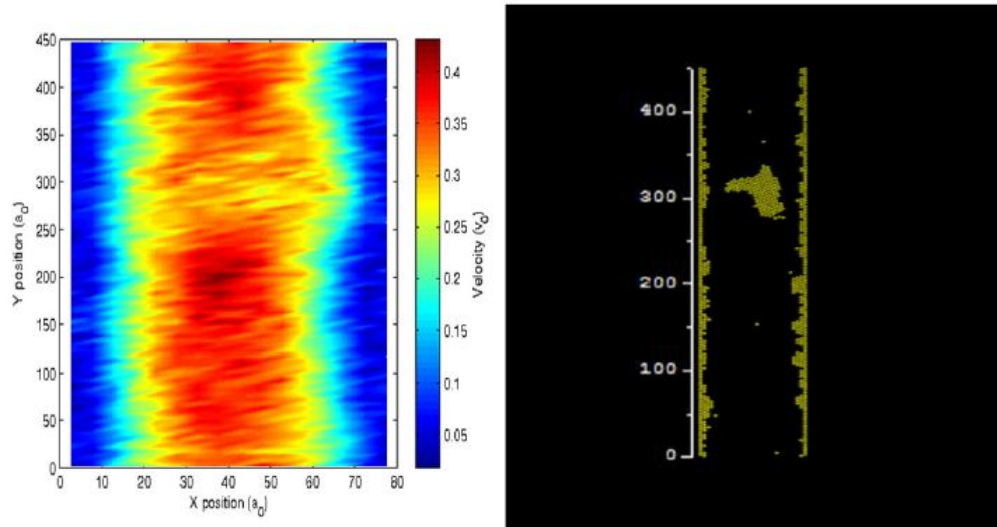


Figure 4.29: SRD simulations of the flow field along the capillary for $Pe = 30$ with the corresponding snapshot at steady state. The colour map highlights the solvent velocity magnitude (Boek et al. 2016).

Laminar flow is most likely to occur in tubes with smooth surfaces at low flow rates and the pressure in this case is directly proportional to the flow and the resistance. However these conditions are not given anymore due to deposits on the wall. Pressure changes within the capillary and local disturbances in the flow profile may interfere with the linear relationship between pressure and flow rate. In fact, in this work here, the resistance seems to decrease with an increase in flow rate, possibly due to the different axial deposition profiles, similar to Figure 4.23. The heterogeneous deposition profile might have an higher impact on resistance, whereas fluid flow may occur less hindered when the flocs deposit more homogeneously.

(B:) THE SHAPE OF THE DEPOSITS: Advection transports the particles towards the deposition surface in forms of irregular flocs. Second, the particles are transported across a boundary layer due to diffusion. It is likely that the second stage predominately controls the deposition process. The disappearance of particles able

to deposit at lower flow rate is caused by floc growth due to collision with other particles. Under given flow conditions, deposition is hindered by a critical particle size, above which deposition is limited, as hydrodynamics outweigh the adhesion forces. Additionally, surface roughness of the particle affects the likelihood of detachment, as the contact area between the particle and the surface decreases. The reduced contact area for the irregular flocs at the lower flow rate is schematically illustrated in Figure 4.30.

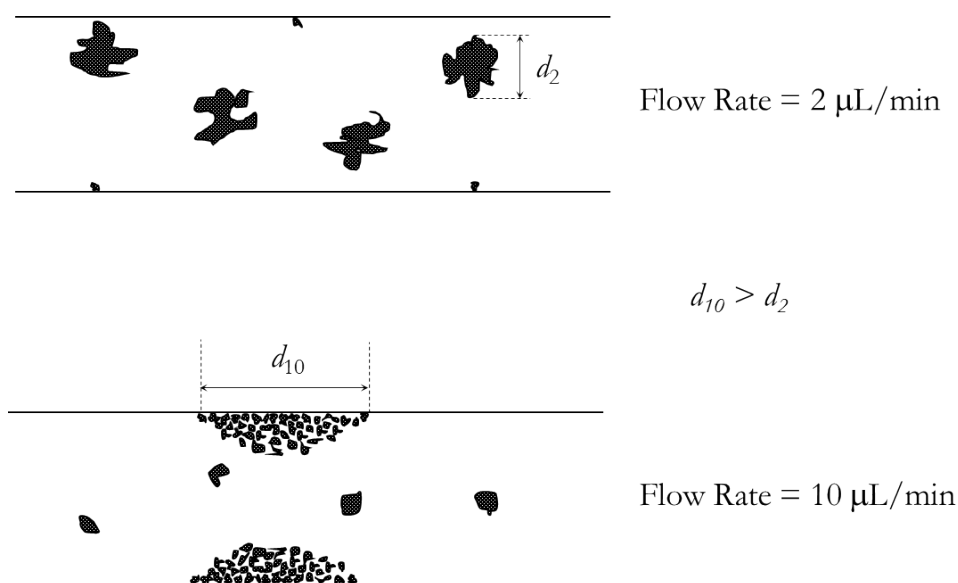


Figure 4.30: Asphaltene floc and deposit shape at different flow rates. The sketch only serves as illustration purposes and does not represent the actual length scales.

On the contrary, smaller particles experience less drag at higher flow rate and an asphaltene floc can build up on the wall. The deposited floc can be considered as a highly porous aggregate composed of smaller ones. The fractal structure of the floc can result in reduced drag by allowing advection of the fluid through the loose structure, which results in a compaction of the flocs causing deformation into a possible “dome shaped” three-dimensional structure (Figure 4.30, bottom sketch).

It is apparent that a higher effective shear stress has a more pronounced effect on floc size, density and structure than at lower flow rate, which can finally lead to

a higher compaction and a more flattened “dome” structure.

The rearrangement of flocs depending on shear delivers a qualitative explanation of why the deposit layer thickness decreases at higher flow rate, thus increasing the hydraulic diameter of the capillary even though more deposition occurs.

(C:) THE DEPOSITION PROFILE: The net mass transport of flocs from the suspension to the capillary wall occurs due to a concentration gradient between surface and solvent at infinite distance in the bulk. In attempts to explain the pressure drop-flow rate relationship, the effective diffusive boundary layer theory can be utilised. Even at low velocities, mass transport in the bulk is convective. Near the surface, the liquid velocity is almost zero and the transport occurs mainly due to molecular diffusion. Within the diffusive layer δ_{Boundary} the concentration change can be approximated to be linear and the diffusive mass flux in terms of particle weight fraction can be expressed as (Grijseels et al. 1981):

$$j = -D \frac{\partial(\rho_{\text{mixture}} w)}{\partial \delta_{\text{Boundary}}} \quad (4.25)$$

where, j = diffusive mass flux of the particles in the suspension; δ_{Boundary} = diffusive boundary layer thickness; w = mass fraction of particles in the suspension

With,

$$w = \frac{\rho_p}{\rho_{\text{mixture}}} C_A \quad (4.26)$$

where, ρ_p = particle density; C_A = volume fraction of particles in the suspension

Levich and Technica (1962) defined for the diffusive boundary layer in a tube with a fully developed Poiseuille flow:

$$\delta_{\text{Boundary}} = 1.47 D^{1/3} \left(\frac{r}{v} \right)^{1/3} x^{1/3} \quad (4.27)$$

where, r = radius of the tube; v = mean fluid velocity; x = distance along a surface

And for the diffusive flux:

$$j = 0.68D^{2/3}\partial(\rho_{\text{mixture}}w)\left(\frac{v}{r}\right)^{1/3}x^{-1/3} \quad (4.28)$$

Levich and Technica (1962) asserts that the thickness of this layer increases substantially along the direction of flow; resulting in a smaller concentration gradient. With an increase in flow rate, the boundary layer becomes thinner and longer such that more particles are able to deposit and further away within the capillary.

The findings here, however, indicate a different dependence of the diffusive flux on the velocity instead of showing a proportionality to $v^{1/3}$. The following paragraph aims to support this underlying assumption.

According to the Stokes-Einstein relationship (Equation (4.3)), the diffusion coefficient is inversely proportional to the particle length scale. Further, the DLS measurements have revealed that (Equation (4.22)):

$$Q_t^2 = A^2v^2 \propto \frac{1}{d} \quad (4.29)$$

Combining these two expressions yields a relationship between diffusion coefficient and velocity as follows:

$$v^2 \propto D \quad (4.30)$$

Substituting this into the definition for the diffusive flux, shows a proportionality to

the square-root of the velocity:

$$j \propto \frac{v^{1/3}}{v^{2/3}} = v^{0.5} \propto \delta_{\text{Boundary}}^{-1} \quad (4.31)$$

Equation (4.31) indicates that the diffusive flux is proportional to $v^{0.5}$ instead of to $v^{1/3}$. The mass flux of particles in the suspension flowing through the capillary, representing the particles able to deposit, is given by:

$$J_w = v\rho w + j \quad (4.32)$$

where, J_w = mass flux of migrating particles in the suspension

The net rate of particle loss caused by deposition is then defined per mass balance:

$$-\dot{m} = \frac{\partial \rho_{\text{mixture}} w}{\partial t} + \frac{\partial J_w}{\partial \delta_{\text{Boundary}}} \quad (4.33)$$

where, $\dot{m}$ = mass rate of particles deposited per unit bulk volume of capillary

Combining Equation (4.31), Equation (4.32) and Equation (4.33) shows the following relationship:

$$\dot{m} \propto v^{0.5} \quad (4.34)$$

This expression states that the mass rate of deposition is proportional to the square-root of the flow rate, which is in agreement with the deposition behaviour at early times as shown in Figure 4.13. The expression was considered to be valid, even though it was constructed from the limiting mass, which depends on both deposition rate and shear removal, and the diffusive flux, which only depends on the deposition

rate. For the subsequent analysis, several assumptions have to be made:

- Every particle diffusing to the wall sticks on to it. This can be considered valid as predominantly sub-micron particles can stick to the wall. The time scale for bigger flocs to diffuse to the wall will be equal or exceeding the residence time in the capillary. The time required for a colloid particle to diffuse over its own radius is defined as:

$$\tau_D = \frac{r^2}{D} \quad (4.35)$$

where, τ_D = diffusion time of a particle

Assuming $r = 1.5 \mu\text{m}$, a value of $\tau_D = 28 \text{ s}$ can be found which is very close to the residence time for the experiment at $Q_t = 5 \mu\text{L}/\text{min}$ (Table 4.3).

- The increase in flow velocity due to the restricted pathway caused by the deposits is considered to be negligible; hence $v \propto Q_t$.
- Equation (4.34) is only valid for the transient pressure drop data. The thickness of deposit layer eventually is limited at steady pressure as entrainment comes into effect. As the limiting mass also depends on the square-root of the flow rate (Figure 4.17) and both transient and steady state pressure drop data collapse on a master curve (Figure 4.14), this relationship was considered to be applicable for subsequent analysis.
- The thickness of the boundary layer increases in x -direction and decreases with flow rate; at a given distance x the boundary layer needs to be thin enough to ensure a high enough concentration gradient for deposition to occur. This distance is assumed to increase linearly with flow rate.
- Deposition occurs homogeneously along the distance x from the capillary inlet.

Having established the above relationships and accounting for an increase in mass with square-root of the flow rate results in:

$$\begin{aligned} \dot{m} &\propto v^{0.5} \propto x \propto \delta_{\text{Boundary}}^{-1} \\ \therefore \frac{\dot{m}}{x} &\propto v^{-0.5} \end{aligned} \quad (4.36)$$

This relationship states that, even though mass deposition flux is higher with increasing flow rate, the deposition per unit area decreases with flow rate. This is in agreement with the findings above, where instead of preferentially depositing at the capillary inlet at $Q_t = 10 \mu\text{L}/\text{min}$, the asphaltenes deposit more homogeneously across the length of the capillary when being in the shear-limited regime (Figure 4.26). The theory established is further highlighted in Figure 4.31, showing the deposition profile based on the change of length and thickness of the diffusive boundary layer.

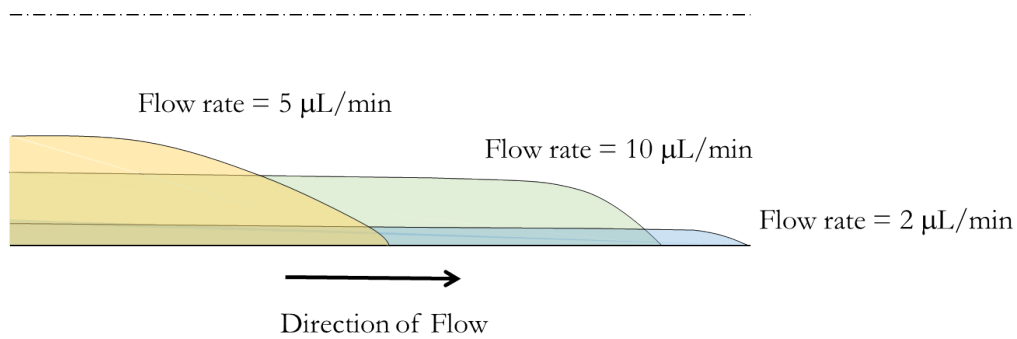


Figure 4.31: Change in deposition profile with flow rate. The dashed-dotted line indicates the middle of the capillary. The sketch only serves as illustration purposes and does not represent the actual length scales.

An anomaly is the lowest flow rate of $Q_t = 2 \mu\text{L}/\text{min}$, for which the deposition occurs homogeneously (Figure 4.16). Having established the concept of the critical particle size, above which a net flux to the wall generated by the concentration gra-

dient cannot be achieved, indicates that the mean floc size generated at that flow rate might be above the threshold. However, asphaltene aggregates in the flow span a large size range and constitute a polydisperse suspension. A large portion of particles are formed from the break up of larger particles into smaller ones or from the growth through aggregation. The smaller sub-micron sized particles are therefore still diffusing to the wall, even though the fluid is depleted of bigger particles able to deposit. With a lower size distribution variability the deposition might occur more homogeneously and additionally the high residence time provides more time available for the particles to diffuse to the wall without being entrained in the flow.

(C1:) THE CHANGE IN DEPOSITION PROFILE DUE TO ENTRAINMENT: In addition, some of the deposits are removed from the wall vicinity due to drag (Figure 4.26), and may then deposit again towards the end of the capillary. Furthermore, at higher shear the flocs travel further down the capillary per unit time before they are able to deposit.

Figure 4.32 summarises the different theories established regarding the distinction between the deposition regimes and how entrainment can affect the deposition profile.

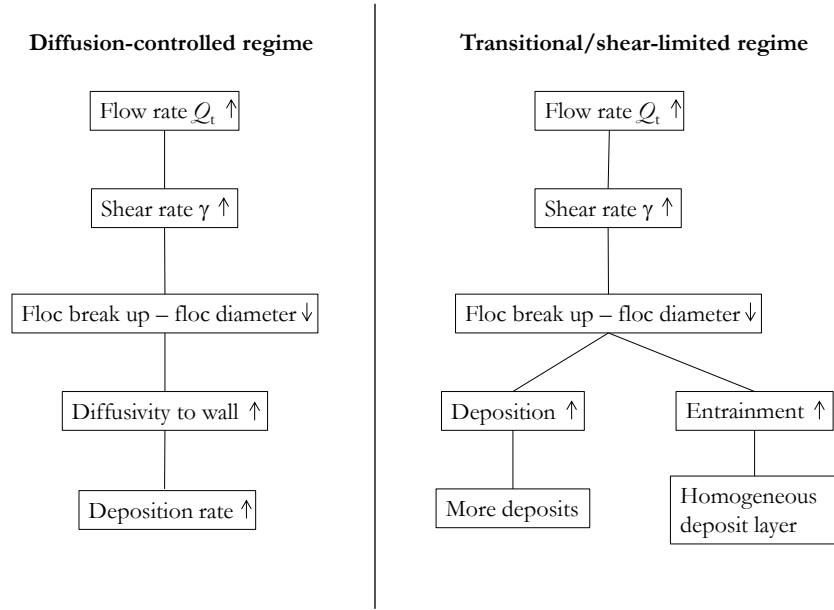


Figure 4.32: Schematic comparison between shear-limited and diffusion-controlled deposition regimes.

4.3.11 The Homogeneous Deposition Model

Given the high aspect ratio of the capillary, the pressure drop in a rectangular channel of a single liquid phase in laminar flow was considered here instead of applying the Hagen-Poiseuille equation. Papanastasiou et al. (1999) developed an expression for two-dimensional Poiseuille flow in tubes of rectangular cross section, illustrated in Figure 4.33.

The analytical solution for steady, pressure driven flow of an incompressible Newtonian fluid in an infinitely long tube of rectangular cross section is given in:

$$u_x(y, z) = -\frac{1}{2\mu} \frac{\partial p}{\partial x} c^2 \left[1 - \left(\frac{z}{c}\right)^2 + 4 \sum_{k=1}^{\infty} \frac{(-1)^k}{\alpha_k^3} \frac{\cosh\left(\frac{\alpha_k y}{c}\right)}{\cosh\left(\frac{\alpha_k b}{c}\right)} \cos\left(\frac{\alpha_k z}{c}\right) \right] \quad (4.37)$$

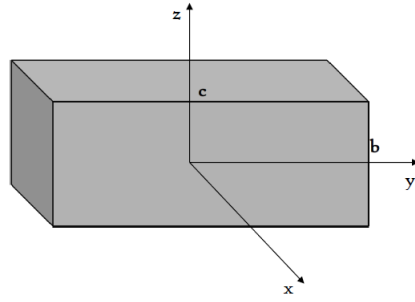


Figure 4.33: Two dimensional Poiseuille flow in a tube of rectangular cross section. c and b are the capillary height and width, respectively.

where,

$$\alpha_k = (2k - 1)\frac{\pi}{2}, k = 1, 2, \dots \quad (4.38)$$

Therefore, the volumetric flow rate is:

$$Q_t = -\frac{4}{3\mu} \frac{\partial p}{\partial x} bc^3 \left[1 - \frac{6c}{b} \sum_{k=1}^{\infty} \frac{\tanh\left(\frac{\alpha_k b}{c}\right)}{\alpha_k^5} \right] \quad (4.39)$$

Assuming homogeneous deposition with a layer thickness of $h/2$ (comparable to e_t as described in Section 2.4.1.1) (Figure 4.34), the pressure drop at varying layer thickness's at constant flow rate can be calculated. The resulting fit can then be used to correlate the layer thickness from the experimental pressure drop. An example for $Q_t = 2 \mu\text{L}/\text{min}$ is shown below in Figure 4.35.

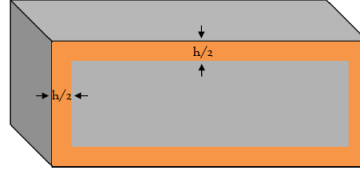


Figure 4.34: Deposit layer thickness $h/2$ in a tube with rectangular cross section assuming homogeneous deposition.

$$Q_t = -\frac{4}{3\mu} \frac{\partial p}{\partial x} (b - h)(c - h)^3 \left[1 - \frac{6(c - h)}{(b - h)} \sum_{k=1}^{\infty} \frac{\tanh\left(\frac{\alpha_k(b - h)}{(c - h)}\right)}{\alpha_k^5} \right] \quad (4.40)$$

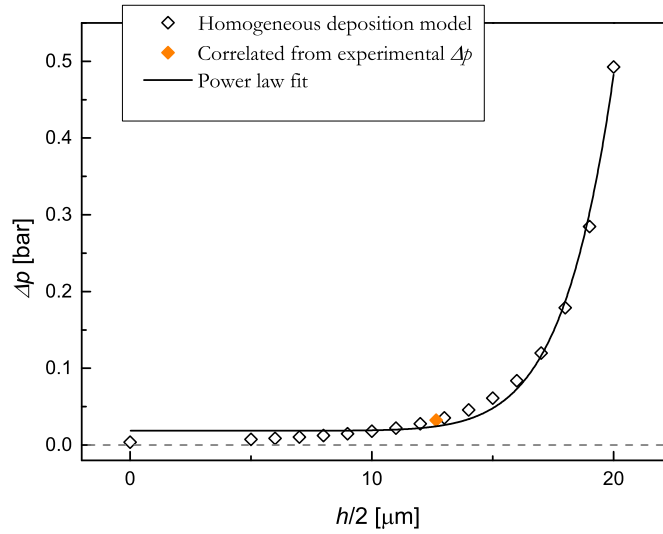


Figure 4.35: Theoretical pressure drop with varying deposit layer thickness and correlated experimental layer thickness at $Q_t = 2 \mu\text{L}/\text{min}$ taken from the pressure drop at steady state. $k = 1, 2, \dots, 100$.

The above described procedure was repeated for the flow rates listed in Table 4.6. The asphaltene density, estimated by Lawal et al. (2012), ($\rho_{\text{asphaltenes}} = 1.16$

g/cm^3) was then used to predict the mass of deposited asphaltenes. The correlated mass from the homogeneous deposition model is compared to the actual mass in Figure 4.36.

Table 4.6: Deposit layer thickness $h/2$ and mass of deposited asphaltenes assuming homogeneous deposition.

Flow rate Q_t [$\mu\text{L}/\text{min}$]	Δp [Pa]	$h/2$ [μm]	$m_{\text{asph.}} \times 10^3$ [g]
2	3230	12.65	0.13
5	5407	10.90	0.11
7	6188	9.91	0.10
10	7476	9.06	0.10
12	7851	8.34	0.09
25	10857	5.93	0.06
60	19616	4.05	0.04
80	20685	2.37	0.02

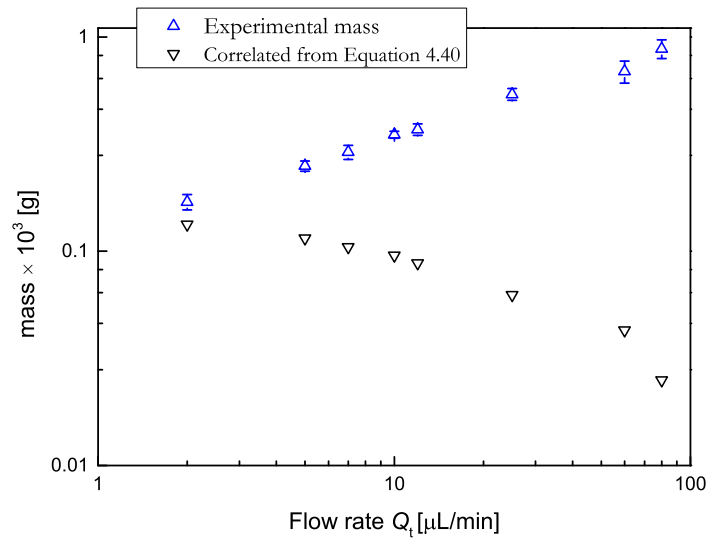


Figure 4.36: Experimentally determined mass of deposited asphaltenes as a comparison to the calculated mass assuming homogeneous deposition.

The correlated mass shows a reverse trend to the actual one; it decreases with

increasing flow rate. This trend, however, is to be expected considering the net decrease in pressure drop with higher flow rate, as the pressure drop data suggest increasing conductance of the capillary with higher flow rate. The results confirm that the homogeneous deposition model cannot be applied to the findings here.

Even though the asphaltenes deposit more homogeneously in the shear-limited regime, the model cannot represent these conditions as the deviations become more pronounced with higher flow rate. The complex hydrodynamics and a possible change in floc density may have further affected the pressure drop.

4.4 Chapter Conclusions

This chapter aimed to close some of the gaps in the literature related to asphaltene deposition in capillary flow. The deposition was studied in a glass capillary, which allowed for visual observation, through pressure drop measurements. The transport of asphaltenes in a capillary follows a multi-step process: Asphaltenes precipitate from the crude oil, aggregate to bigger flocs, deposit onto the surface, break up into smaller flocs and experience advection and entrainment due to shear. Being in the diffusion-controlled regime, the floc break up dominated over further shear-induced aggregation. The smaller floc size led then to more deposits adsorbing on the wall with higher flow rate, as the floc size is inversely proportional to the diffusion coefficient. Once a deposit layer has been formed, it was maintained as long as the adhesive forces were greater than the removal forces. At a particular deposit thickness, a dynamic equilibrium eventually led to a steady state condition in terms of the pressure drop.

The deposition profile in the direction of flow was found to be highly non-uniform, as more deposition was observed near the capillary inlet. Increasing the flow rate further, entering the shear-limited region, seemed to spread out the deposition more

homogeneously as the higher shear caused entrainment from the loose deposit layer into the bulk. At the same time the deposition rate was slower than for deposition in the diffusion-controlled regime. These findings were confirmed by SRD computer simulations. The change in hydrodynamics, due to the lumpy deposit layer, may have caused a disruption from the laminar flow profile into a plug flow type behaviour, causing a deviation from the linear pressure drop and flow rate relationship which was found to be valid in the empty capillary.

Chapter 5

Asphaltene Deposition in Porous Media

5.1 Introduction

Asphaltene deposition in porous media, resulting in permeability impairment, is one of the major issues in the oil industry. The deposits may damage the rock by blocking the pore throats and pore bodies. The main factors under which asphaltene deposition occurs are still subject to research in the literature.

In this project a series of core-flooding experiments are conducted to investigate the effect of asphaltene deposition on permeability in two sandstone samples Berea and Bentheimer. Firstly, C7-asphaltenes in toluene are re-precipitated with *n*-heptane at ambient conditions and in further experiments crude oil asphaltene deposition, initiated by CO₂, are studied at conditions similar to reservoir temperature and reservoir pressure. The permeability damage is assessed through pressure drop measurements and subsequent combined microCT imaging and lattice-Boltzmann calculations. Three mechanisms contributing to asphaltene damage in porous media are presented: Surface deposition, entrainment and pore throat plugging. Wang

(2000) and Wang and Civan (2001) suggested a four-parameter equation for the net deposition rate of asphaltenes, described here as the Deep Bed Filtration model. These equations are implemented in the reservoir modelling tool ECLIPSE 300 and are used as an empirical fit to the experimental data.

5.2 Materials and Methodology

5.2.1 Experimental Set-up

5.2.1.1 Asphaltenes in Toluene and Heptane

For the studies at ambient conditions, C7-asphaltenes were dissolved in toluene at a concentration of 1 g/L and then co-injected with *n*-heptane through the rock sample at a ratio of heptane to toluene of 3:1. In the capillary flow experiments this ratio was found to give sufficient asphaltene precipitation and deposition while ensuring a detectable range of change in pressure drop.

A schematic diagram of the core-flooding set-up is shown in Figure 5.1. The rock samples studied (Berea and Bentheimer sandstone) were drilled into cylindrical cores 6 mm in diameter and 17 - 18 mm in length. The cores were dried in the oven to evaporate the remaining moisture; no further treatment was then carried out. These samples were placed within a fluoro-polymer elastomer (Viton) sleeve and subsequently attached to stainless steel (SS) fittings connecting the core to the inlet and outlet fluid flow lines. This assembly was placed in a high pressure-high temperature SS type flow cell designed and built *in-house*. Further details about the design are presented below. The flow lines were made of PEEK (1533, Kinesis, U.K.) and the inlet flow lines were connected to the pumps (Quizix, QX Series, Ametek Chandler Engineering, U.S.). The fluid streams mix at the inlet core holder endcap before entering the rock sample. Two pressure transducers (#PXM319-350G1, 4-

20 mA, Omega Engineering Ltd, U.K.) were used to measure the inlet and the outlet pressure ($p_{\text{inlet}} - p_{\text{outlet}} = \Delta p$). A confining pressure in the range of 1000 PSI was set, using a handpump (P-39, Enerpac, U.S.) filled with hydraulic oil (HF-100, Enerpac, U.S.). The confining fluid pressure was measured with a pressure gauge (#PGS-35L-10000, Omega Engineering Ltd, U.K.) and was used to compress the Viton sleeve around the rock sample, which prevents fluid from bypassing between the sleeve and the rock sample. The outgoing fluids and precipitated, but not deposited, asphaltenes were collected in a beaker. No back pressure was used in the experiment.

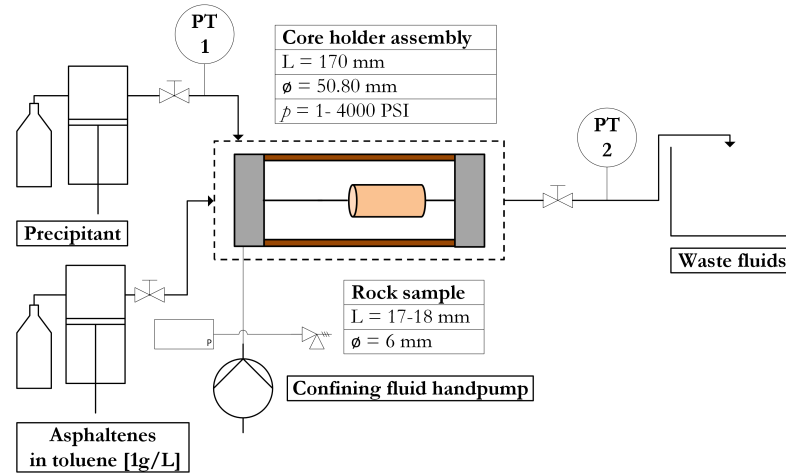


Figure 5.1: Schematic diagram for the experimental core-flooding set-up. Heptane was used to precipitate asphaltenes from a toluene solution [1 g/L].

5.2.1.2 Diluted Crude Oil and CO₂

Next, asphaltene deposition induced by CO₂ was studied for which a fluid mixture, previously studied in Chapter 3, was chosen: Zuata crude oil was diluted with 30 wt% of toluene to reduce the crude oil viscosity and make the experiments more practical to carry out. For this mixture the amount of precipitated asphaltenes and the solubility of CO₂ in the oil is known at a given temperature and pressure.

To ensure asphaltene precipitation, the pressure had to be greater than 100 bar. According to the solubility measurements at equilibrium with CO_2 , the system exhibits multiphase behaviour in this pressure region. To minimise potential phase separation in the core-flooding experiments, which would lead to problems interpreting the pressure drop measurements in terms of asphaltene deposition, the weight fraction of injected CO_2 ($w_{\text{CO}_2} = 0.170$) was set slightly below the equilibrium weight fraction ($w_{\text{CO}_2} = 0.187$). Furthermore, it was assumed that precipitated asphaltenes do not change the phase boundary.

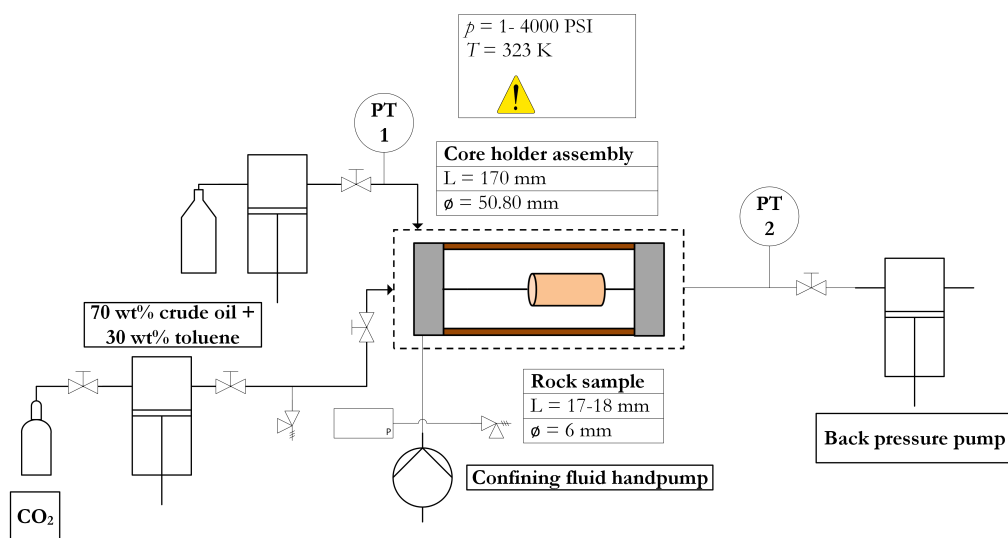


Figure 5.2: Schematic diagram for the experimental core-flooding set-up. CO_2 was used to precipitate asphaltenes from a 70wt% crude oil+30wt% toluene mixture.

To prevent diffusive exchange of CO_2 across the Viton sleeve, the rock sample was wrapped into aluminium foil before placing it within the sleeve. Previously, this method has proven to be effective as shown by Andrew et al. (2014). A temperature of $T = 323 \text{ K}$ in the flow cell was maintained through a heating tape (#SRT051-60, Omega Engineering Ltd, U.K.) and a thermocouple (#4094908, K-Type, RS Components Ltd, U.K.) wrapped around the body of the coreholder connected to a custom built PID controller (Electrical Workshop, Department of Chemical En-

gineering, Imperial College London). The basic experimental set-up remained the same, however, with a few adjustment to account for high pressure and temperature. The Quizix pump, previously used for heptane displacement, was exchanged for a syringe pump (ISCO #100-D, U.S.) which was filled with CO₂ and set at the desired pressure. Instead of collecting the waste fluids in a beaker, the oil and CO₂ were set to flow into a back-pressure pump (ISCO #500-D, U.S.), which was set at constant pressure to regulate the pressure at the coreholder outlet. The previously used PEEK fluid tubings were exchanged for stainless steel 1/16" tubing to be able to withstand the high pressure and material compatibility. The confining fluid pressure was adjusted to be approximately 20 bar above the pressure for each experiment.

5.2.2 The Coreholder Design

A key requirement for the design of the core holder was the resistance to high pressure and high temperature (HPHT) conditions. The core-flooding experiments were carried out at similar conditions to the filtration and solubility measurements at $T = 298$ K and $T = 323$ K and within a pressure range from ambient to 150 bar. In order to withstand this conditions, stainless steel was chosen as the material and the main body and two end caps were designed with the necessary thickness. The rock samples to be studied were drilled into 6 mm cores with a length of approximately 17-18 mm. To fit the sample and required fittings comfortably into the core holder, the length of the main body was 100 mm. Similar to the capillary flow experiments, the set-up should allow for co-injection of the asphaltene solution and the precipitant to avoid asphaltene deposition in the flow lines.

Prior to any experiments, the core holder was pressure tested up to 350 bar by flooding heptane through a rock sample and increasing the back-pressure in increments of 20 bar. To avoid over pressurising the assembly in the experiments,

the safety pressure was set to 180 bar at the pumps used and a pressure relief valve (#SS-4R3A, with Red Spring Kit, 4000-5000 psig, Swagelok, U.K.) was built in between pumps and core holder. The weakest part in the system was identified as the nitrile O-rings used to seal the gap in between the end caps and the main body.

The core holder was designed using SolidWorks Education Edition 2012-2013 (Figure 5.3) and then manufactured by the Mechanical Workshop, Department of Chemical Engineering, Imperial College London. The technical drawings for the three different parts (main body, end cap - inlet and end cap - outlet) are shown in Figure D.1, Figure D.2 and Figure D.3, respectively.

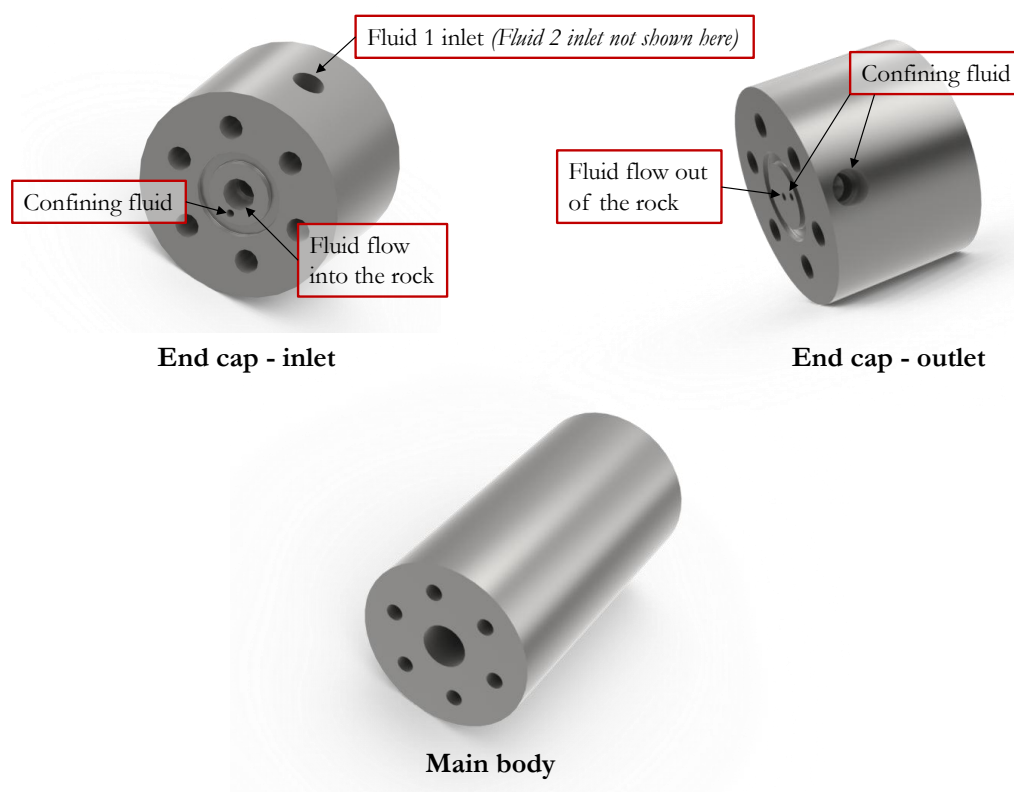


Figure 5.3: 3D visualisation of the designed coreholder. The three parts are connected through M6 screws.

5.2.3 The Choice of Flow Rates

The asphaltene containing fluid (toluene or diluted crude oil) flow rates were chosen to represent oil velocities during production close to the well-bore regions (typically one to several m/day), while still ensuring laminar flow. Table 5.1 summarises the flow rates used in the two sandstones. The volumetric flow rates were converted into the interstitial velocity using the superficial velocity and the rock porosity. To assure laminar conditions, the Reynolds number was calculated for the fluid flow through the porous medium. The average pore diameter required for the calculations were taken from Shah et al. (2015). In their work, three dimensional pore-scale microCT images from selected rock samples were reconstructed, from which the petrophysical properties were computed with LB and Pore Network simulations. Injecting the toluene solution at the desired flow rates results for Re to be in the range of 10^{-3} (Bentheimer) and $10^{-3} - 10^{-4}$ (Berea), whereas for the more viscous diluted crude oil, Re decreased to 10^{-6} in Bentheimer.

Table 5.1: Volumetric flow rates and interstitial velocities for the diluted crude oil and the asphaltenes in toluene solution. The flow rates were converted into the velocity by using the rock's porosity.

	Asph. flow rate [$\mu\text{L}/\text{min}$]	Interstitial velocity [m/day]
Bentheimer	5	1.32
	12.5	3.29
	25	6.59
	50	13.17
	100	26.34
Berea	5	2.19
	25	10.94
	37.5	16.41
	125	54.87

5.2.4 Setting up the Pressure Transducers

5.2.4.1 Pressure Calibration

The pressure transducers at the core holder inlet and outlet were calibrated at a pressure range from 1 - 350 bar with a quartz pressure sensor in a pneumatic calibrator (Fluke-DHI PPCH-G-70M). The pressure was increased from 1 - 350 bar and then decreased downwards from 350 - 1 bar. For each step (increment: 10 bar and above 100 bar: 20 bar) the output as electrical current was measured for both transducers. The transducers exhibit a good linearity for the averaged output, shown in Figure E.1.

5.2.4.2 Pressure Drop Measurement with LabVIEW

The program to measure the pressure drop was written in LabVIEW, which is a graphical programming environment. A snapshot of the block diagram window is shown in Figure 5.4. The controls were built in the front panel, including start/stop button and the option to enable data writing into a *.lvm* file. The codes for the front panel were written into the block diagram using **virtual instruments** and structures to control the front panel objects. A major component in the block diagram is the DAQ Assistant, which communicates with the data acquisition hardware (NI 9219, National Instruments), connected to the two pressure transducers. The icon “Build XY graph” writes the measured pressure into a graph as a function of time. Simultaneously, the pressure drop is calculated by subtracting the inlet from the outlet pressure. The index array function allows for the correction of each pressure transducer after its calibration.

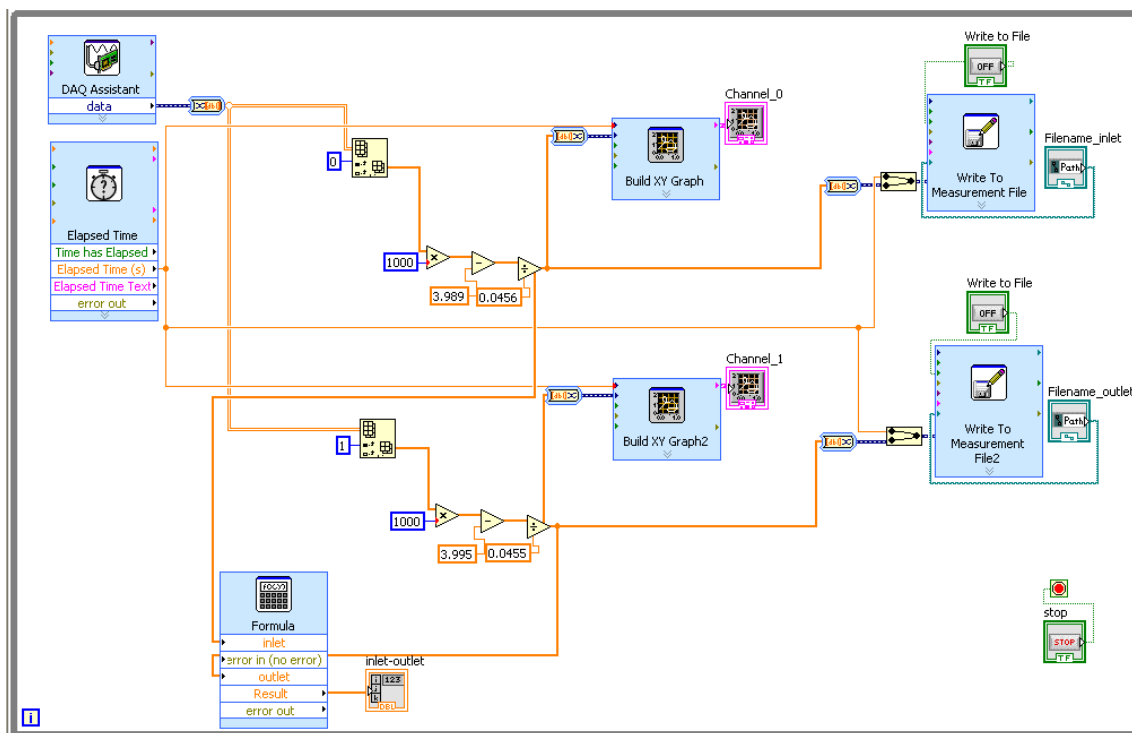


Figure 5.4: LabVIEW block diagram showing all necessary virtual instruments to measure the pressure drop.

5.2.5 X-Ray Microtomography Imaging

5.2.5.1 Image Acquisition

The dry and wet rock samples were scanned using a Versa XRM-500 X-Ray Microscope (Zeiss X-Ray Microscopy, Pleasanton, CA, U.S.). To scan the wet sample, the core holder was disassembled and the rock core removed from the Viton sleeve. The sample was then mounted onto a stage designed to fit into the microCT. To support the core on the stage, “Blu-Tack” was used as an adhesive which can be easily removed after scanning while at the same time firmly attaches the sample to

the stage.

The scans were taken at a voltage of 80 kV with a power of 7 W. The detector and source distance were chosen to obtain the desired voxel size at the optimum exposure time. 3D images were then reconstructed using the XMReconstructor by Zeiss from a set of 3200 projections. An example of a reconstructed image can be seen in Figure 5.5.

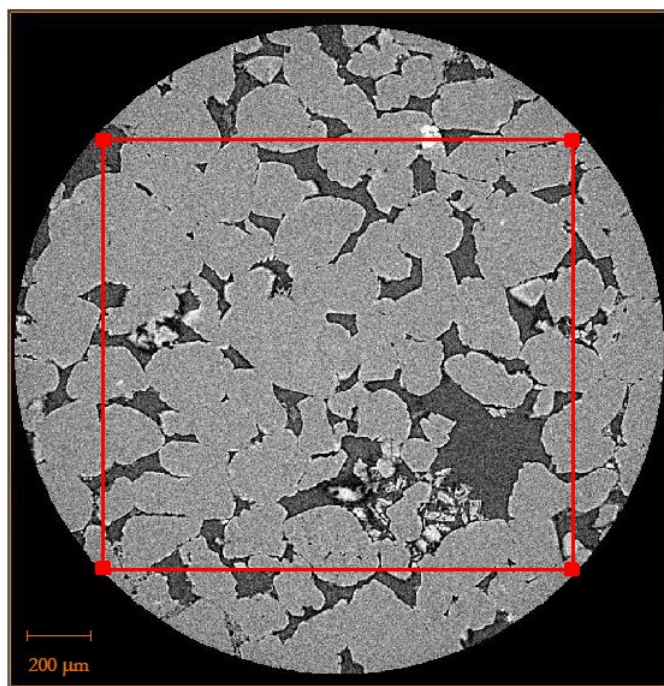


Figure 5.5: Reconstructed slice (110 of 992) from a Bentheimer rock sample, scanned at a voxel resolution of $2.1 \mu\text{m}$.

For the data analysis two different voxel sizes ($8.6 \mu\text{m}$ and $2.2 \mu\text{m}$) were chosen. A voxel size of $8.6 \mu\text{m}$ allows for scanning almost the entire cross diameter of the rock sample, while the higher resolution allows for a more detailed analysis in terms of resolving pores and asphaltene deposits. Each section scanned consisted of around 1000^3 voxels. For the lattice-Boltzmann (LB) analysis (described below), the image was cropped into a cuboidal volume of approximately $430 \times 450 \times 580$ voxels ($8.6 \mu\text{m}$) and $650 \times 700 \times 990$ voxels ($2.2 \mu\text{m}$) which results in a real image size of approximately

$4 \times 4 \times 5$ mm ($8.6 \mu\text{m}$) and $1.4 \times 1.5 \times 2.2$ mm ($2.2 \mu\text{m}$), respectively. The biggest crop possible was chosen to capture most of the image; an example box is displayed in Figure 5.5. The edge of the crop box was registered with the inlet phase of the core.

5.2.5.2 Image Processing

After image acquisition, the image was processed with the software Avizo Fire 8.0 and Avizo 9.0.0 (Visual Science Group, Burlington, MA, U.S.). An example workflow for Bentheimer (voxel size = $2.1 \mu\text{m}$) is shown in Figure 5.6. A subvolume was extracted from the reconstructed image (Figure 5.6) to which the LB analysis was restricted to. The images were filtered using a non-local means edge preserving filter. The images were then segmented into two phases, with the pores being treated as one phase and the grains treated as the other phase. For the segmentation a watershed algorithm was applied, computed off a seed which was generated using a 2D histogram.

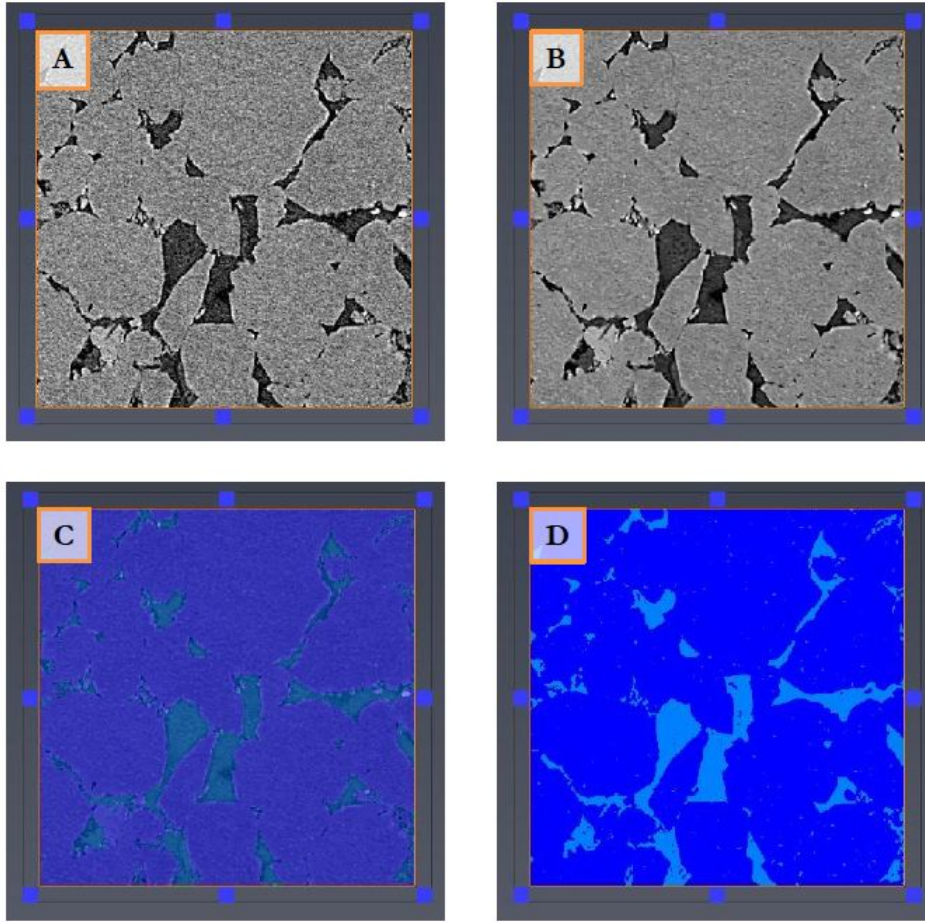


Figure 5.6: Avizo workflow example for segmentation of a dry image, here shown for Bentheimer (voxel size = $2.1 \mu\text{m}$). **A**: Extracted subvolume ($500 \times 500 \times 500$ lattices) from original reconstructed image. **A-B**: The image was filtered using a non-local means filter. **B-C**: Mapping from the seed region generated using 2D histogram. Each coloured region represents a different seed region. Only the low gradient information were used as seed regions. The light blue regions correspond to pores and the royal blue ones to grains. **C-D**: Each voxel outside the seeded region was assigned to one of the two phases using a watershed algorithm.

5.2.6 Lattice-Boltzmann (LB) Modelling

The LB single phase calculations were performed to determine the permeability and porosity at the chosen voxel sizes. The model describes the hydrodynamics of a fluid in terms of a distribution function which represents the fraction of fluid

particles at a given position with a particular velocity. The distribution function evolves according a discrete version of the Boltzmann equation whereby particle collide in the fluid and stream according to their velocity and can be shown to recover the incompressible Navier-Stokes equations (Chen et al. 1992). Here, the 3D, 19-velocity vector (D3Q19) lattice in conjunction with the multiple-relaxation-time (MRT) collision operator and bounce-back boundary conditions at the solid-interface are used (Qian et al. 1992; D’Humières 2002), which gives accurate values of absolute permeability in complex porous media (Shah et al. 2015). The model was implemented on GPU for optimal performance (Gray and Boek 2016).

The segmented image slices were saved as a stack of *tiff* files and then converted to a file format which can be read by the code (*.dat*). This geometry file is mirrored in the direction of the flow (here: *z*-direction) to give continuous loop boundaries. The mirrored geometry file then runs on the cluster, performing the calculations on the GPU nodes. A uniform body force is applied to the fluid and the calculation is iterated until the flow field reaches steady state. Finally, the permeability is obtained from Darcy’s law.

5.2.7 Deep Bed Filtration (DBF) Modelling

The Deep Bed Filtration (DBF) model was used to fit the experimental pressure drop data, thus allowing for additional analysis of the mechanism in terms of the asphaltene formation damage caused by deposition. The simulations were run in the **ECLIPSE 300** reservoir simulator using the “Asphaltene Option”, which implements the equations in the DBF model described by Wang (2000), Wang and Civan (2001), and Wang and Civan (2005). The rate equations for surface deposition, entrainment and plugging contributing to the net deposition rate $\partial E_A / \partial t$ are defined by Wang and Civan (2001) and Wang and Civan (2005) as follows:

$$\frac{\partial E_\alpha}{\partial t} = \alpha C_A \phi \quad (5.1)$$

where, α = surface deposition coefficient; C_A = volume fraction of particles in the flowing suspension; ϕ = porosity

$$\begin{aligned} \frac{\partial E_\beta}{\partial t} &= \beta E_A \\ \beta &= \beta_i(v_L - v_{L,cr}), \text{ when } v_L > v_{L,cr} \\ \beta &= 0, \text{ when } v_L < v_{L,cr} \end{aligned} \quad (5.2)$$

where, β = entrainment coefficient; E_A = volume occupied by deposited particles; v_L = interstitial velocity through porous medium, the subscript *cr* denotes the critical value

$$\begin{aligned} \frac{\partial E_\gamma}{\partial t} &= \gamma \phi C_A \\ \gamma &= \gamma_i(1 + \gamma_j E_A) u_L, \text{ when } D_{pt} < D_{pt,cr} \\ \gamma &= 0, \text{ when otherwise} \end{aligned} \quad (5.3)$$

where, γ = pore throat plugging coefficient; u_L = superficial velocity through porous media; D_{pt} = mean pore throat diameter, the subscript *cr* denotes the critical value

By enabling the keyword **ASPHALTE** in the simulator, asphaltene formation (e.g. precipitation, flocculation, dissociation, deposition, entrainment) and damage (e.g. porosity, permeability, wettability) can be modelled. Although they are a number of asphaltene models in existence, there is still no consensus about on how to characterise asphaltene behaviour and how to use the ‘‘Asphaltene Option’’ in a predictive way. Asphaltene modelling in ECLIPSE is decomposed into four different stages, which are modelled using different keywords (Figure 5.7). A short introduction about the the different stages is given below, where the most important keywords

are highlighted. An example of the main input file is shown in Section G.1. (*Note:* In ECLIPSE, the precipitated asphaltenes in solution are called *fin*es and the aggregated bigger particles are referred to as *floc*s.)

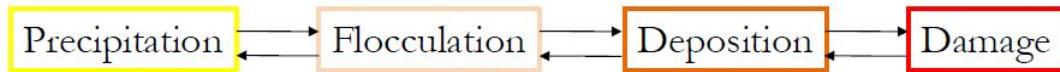


Figure 5.7: Asphaltene modelling stages in ECLIPSE. Precipitation triggers a sequence of flocculation, deposition and subsequently damage. The double arrow indicates reversibility (partial or total).

Asphaltene Precipitation Initially the asphaltenes are dissolved in the oil, and the fines first start appearing once its weight percentage in the oil is above a certain limit, depending on the variable the weight percentage limit (e.g. pressure) is set against. Precipitation does not change the fluid composition and only defines the fraction of asphaltenes which will contribute to the flocculation process. Asphaltenes are defined as a set of components, which can precipitate depending on their weight percentage in solution. The solubility limit is defined in the keyword **ASPREWG**. In conjunction, the keyword **ASPFLOC** is used to define the components which can precipitate. The list of components in the model are enumerated as 1,2,... N , and ASPFLOC is then followed by three integers corresponding to:

- The number of the first component that can precipitate
- The number of the last component that can precipitate
- The number of the component that represents the flocs

The components to be simulated in the model are defined as a character string in **CNAMES**. An example of how the precipitating components are defined to fit the ambient core-flooding data is shown below:

CNAMES

-
- Component Names
-

'Tol'
'C7'
'ASP'
'flocs'

ASPFLOC

3 3 4 /

Asphaltene Flocculation Flocculation is the process where the fines aggregate to bigger flocs. The keyword **ASPFLRT** defines the flocculation and dissociation rates. Due to the lack of further experimental data, both values were set to zero.

Asphaltene Deposition and Entrainment When the dissolved asphaltenes become available as fines, they are available for deposition on the rock surface or become trapped in the pore throats. Depending on the local shear, asphaltenes can also be entrained and returned to the flowing fluid phase. As described in Section 2.5.2, the net rate of asphaltene deposition can be described as: Rate of surface deposition + rate of plugging - rate of entrainment.

From this model, four fitting parameters were chosen and are defined using the **ASPDEPO** keyword: *(i)* the surface deposition rate coefficient α , *(ii)* the entrainment coefficient β , *(iii)* the pore throat plugging coefficient γ and *(iv)* the critical interstitial velocity $v_{L,cr}$. According to Wang (2000), $v_{L,cr}$ and also the critical pore diameter $D_{pt,cr}$ are set as constants. As the DBF model is used as an empirical estimate, the fitting parameters are chosen arbitrarily in a “trial and error” procedure (Wang and Civan 2001). Please note that in the asphaltene model implemented in ECLIPSE 300, $D_{pt,cr}$ is not defined and can only be turned on by setting γ in the plugging rate equation unequal to zero.

Asphaltene Damage The asphaltene damage in the rock sample was modelled as the reduction in absolute permeability as a function of porosity using the **ASPKDAM** keyword:

$$\frac{k}{k_0} = \left(1 - \frac{E_A}{\phi_0}\right)^n \quad (5.4)$$

As described in Section 2.5.2, the value of the exponent n in the power law equation is still debatable. Figure 5.8 shows that a change in the exponent from 3 to 5, whilst keeping the other parameters constant, changes the curve significantly. For consistency purposes, the exponent was set to 3 in all simulations, as described by Civan et al. (1989) and Wang (2000). As further work to improve the fit, a log/log plot of the experimental data of (k/k_0) against $(1-(E_A/\phi_0))$ will help choosing the correct exponent.

Initial and Boundary Conditions Depending on the system studied, the back-pressure had to be defined accordingly: To fit the experiments at ambient conditions, the pressure in the simulation was set to 1 bar and to simulate the HPHT experiments, it was set depending on the pressure studied (140 and 150 bar). Furthermore, the experiments were run at constant flow rate, hence the boundary conditions can be defined as follows:

$$\begin{aligned} u_L &= \frac{Q}{A} \text{ at } x = 0, t > 0 \\ p &= 1 \text{ bar at } x = L, t > 0 \end{aligned} \quad (5.5)$$

where, L = length of the rock sample

It is assumed that no asphaltenes precipitate from the solution before it is mixed

with the precipitant. Thus the following initial conditions can be applied:

$$\begin{aligned}
 C_A &= 0 \text{ at } 0 \leq x \leq L, t = 0 \\
 E_A &= 0 \text{ at } 0 \leq x \leq L, t = 0 \\
 \phi &= \phi_0 \text{ at } 0 \leq x \leq L, t = 0 \\
 k &= k_0 \text{ at } 0 \leq x \leq L, t = 0
 \end{aligned} \tag{5.6}$$

Grid Dimensions The size of the simulation grid was specified in x , y and z -direction by the **DIMENS** keyword. In this case, the reservoir is represented by a $10 \times 1 \times 1$ grid.

Validation of the “Asphaltene Option” using a Literature Data Set

The DBF model in the “Asphaltene Option” was tested against a literature data set (Minssieux 1997). The data set considered was GF3 for a Fointainebleau sandstone with $k_0 = 77.4$ mD and $\phi_0 = 13.7\%$. The Weyburn crude oil (API Gravity = 29), with an asphaltene content of 5.3wt%, was injected through the rock core with a flow rate of $10 \text{ cm}^3/\text{h}$ at $T = 323 \text{ K}$. In Figure 5.8, the permeability change k/k_0 as function of pore volumes (PV) injected is compared to the DBF model fit. It was found that the best fit can be obtained using the surface deposition parameter α only (here: $\alpha = 4 \text{ hr}^{-1}$). This indicates that the surface deposition is probably the dominant process at short time scales, whereas the entrainment rate coefficient β only affect the model at later times (Boek et al. 2011).

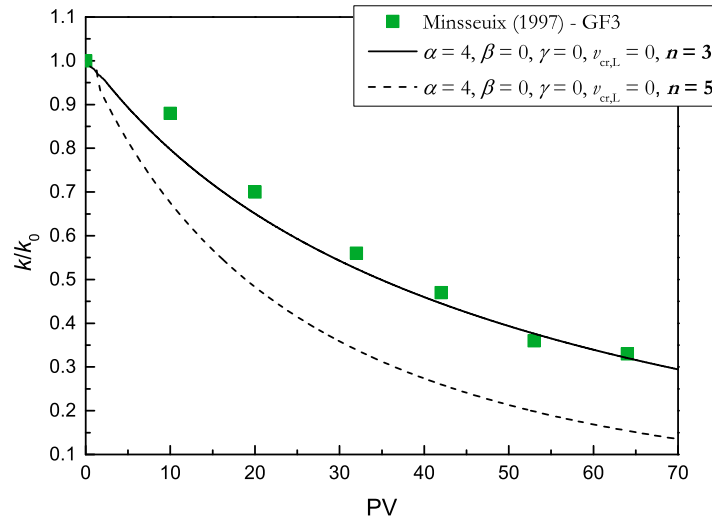


Figure 5.8: Fitting the DBF model to a literature data set. The experimental data were taken from Minssieux (1997).

5.3 Results and Discussion

The results are presented as follows: Section 5.3.1 shows the permeability and porosity calculations for the dry samples via single phase flooding experiments and compares them to subsequent LB calculations. These values were then used to convert the measured pressure drop data from the core-flooding experiments at ambient (Section 5.3.2) and reservoir conditions (Section 5.3.3) into the dimensionless permeability, to which the DBF model was fitted to. Furthermore, asphaltene deposits were visualised using the microCT technique and differences between C7 and CO₂-asphaltenes are highlighted. Finally, limitations and suggested improvements of the DBF model are discussed in Section 5.3.4.

5.3.1 Permeability of the Dry Samples

Prior to any experimental studies it is necessary to determine both permeability and porosity of the dry sample through single phase core-flooding experiments and combined microCT imaging and LB calculations. To measure the permeability of the dry sample ($k_{0,\text{exp.}}$), heptane was injected at ambient conditions at a constant flow rate whilst monitoring the pressure drop across the length of the sample. The rock core was initially saturated with heptane through vacuum immersion. Several flow rates were applied to obtain accurate measurements. From the measured pressure drop Δp , the permeability of the dry sample can be calculated using Darcy's law (Equation (5.7)).

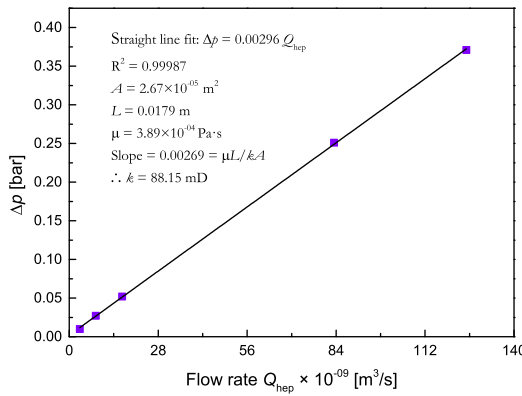
$$k = \frac{Q_t}{A} \mu \frac{L}{\Delta p} \quad (5.7)$$

where, k = permeability [mD] ($1 \text{ Da} = 9.87 \times 10^{-13} \text{ m}^2$); Q_t = total volumetric flow rate; A = cross sectional area of the rock sample; μ = dynamic viscosity of heptane at ambient conditions ($3.89 \times 10^{-04} \text{ Pa}\cdot\text{s}$)

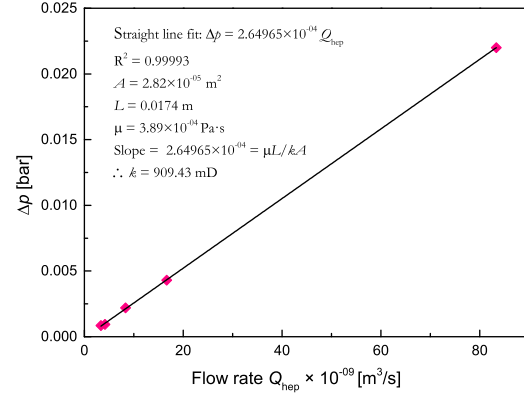
Table 5.2 summarises the applied flow rates and the corresponding pressure drop. The linear relationship between the flow rate and the measured pressure drop (Figure 5.9a and Figure 5.9b) indicates reliable and accurate calculations of the permeability. The straight line fit passes through the origin, that is, if the flow rate $Q_{\text{hep.}} = 0$, then $\Delta p = 0$. The slope of the fit is equal to $\mu L/kA$, which then allows the permeability calculation from the parameters described in Equation (5.7). The calculations for the absolute permeability are shown below. Calculating the permeability through the slope based on the multiple flow rates and corresponding pressures, is a further indication of reliable measurements.

Table 5.2: Applied flow rates, measured pressure drop and corresponding single phase permeability.

	Flow rate [$\mu\text{L}/\text{min}$]	Δp [bar]	permeability $k_{0,\text{exp.}}$ [mD]
Berea	3.33×10^{-10}	0.010	88.13
	8.33×10^{-10}	0.027	81.60
	1.67×10^{-9}	0.052	84.74
	8.33×10^{-9}	0.251	87.78
	1.25×10^{-8}	0.371	89.08
Bentheimer	3.33×10^{-10}	0.00085	957.49
	4.17×10^{-10}	0.00093	1093.91
	8.33×10^{-10}	0.00220	924.85
	1.67×10^{-9}	0.00430	946.36
	8.33×10^{-9}	0.02200	924.85



(a) Berea



(b) Bentheimer

Figure 5.9: Linear relationship between pressure drop and flow rate for single phase runs.

The dry samples were imaged using the microCT technique (Berea: 8.6 and 2.2 μm voxel resolution; Bentheimer: 2.1 μm voxel resolution) to calculate the single phase permeability with LB simulations ($k_{0,\text{LB}}$). Due to the presence of clay in Berea, a three-phase segmentation was performed, where clay was treated as a solid phase. The workflow for a $400 \times 456 \times 463$ subsample to obtain the LB input file is

shown in Figure 5.10.

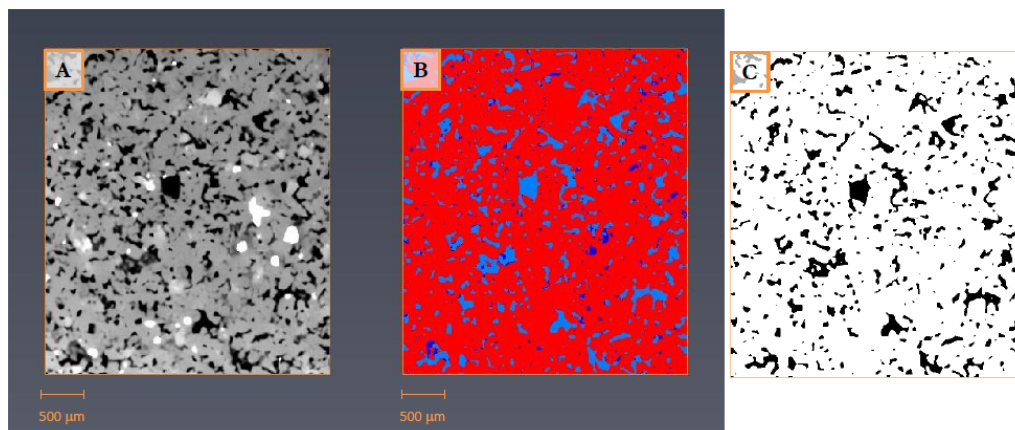


Figure 5.10: Example workflow for Berea sandstone ($8.6 \mu\text{m}$) as an input image sequence for the LB code. **A:** Filtered slice of original raw image. **B:** Applied three phase segmentation; the light blue parts are the pores, the royal blue ones represent the clay and the remaining red parts were segmented as grains. **C:** Binarised image as *tiff* extension.

The experimental porosity was determined through gravimetric analysis by calculating the weight difference from the dry sample and the sample filled with fluid through vacuum immersion. Table 5.3 and Table 5.4 show a good agreement between the theoretical and experimental values for the rock parameters. Three different scans were taken along the length of the sample, the values obtained through the LB calculations were used to calculate a mean value and their standard deviations. If the porosity is connected, scanning the rock sample at a higher resolution will resolve more smaller pores, thus resulting in a higher permeability $k_{0,\text{LB}}$. Discrepancy also results from that the calculations were performed on a different, and much smaller, volume of the rock than the experimental one, where $k_{0,\text{exp}}$ only provides an average value for the permeability. Therefore, by chance, the LB approach results in a higher permeability.

Table 5.3: Experimentally and theoretically determined permeability and porosity for the dry Berea.

Porosity ϕ [%] and permeability k [mD]	Berea
$\phi_{0,\text{exp.}}$	12.28
$\phi_{0,\text{LB}}$ (8.6 μm)	11.57 ± 0.03
$\phi_{0,\text{LB}}$ (2.2 μm)	15.18 ± 0.86
$k_{0,\text{exp.}}$	86.26 ± 3.07
$k_{0,\text{LB}}$ (8.6 μm)	129.79 ± 4.61
$k_{0,\text{LB}}$ (2.2 μm)	232.28 ± 35.31

Table 5.4: Experimentally and theoretically determined permeability and porosity for the dry Bentheimer.

Porosity ϕ [%] and permeability k [mD]	Bentheimer
$\phi_{0,\text{exp.}}$	19.35
$\phi_{0,\text{LB}}$ (2.1 μm)	20.17 ± 0.55
$k_{0,\text{exp.}}$	969.49 ± 70.97
$k_{0,\text{LB}}$ (2.1 μm)	1001.45 ± 12.56

As the Bentheimer will be used in the HPHT experiments, the effect of pressure on the permeability was tested by flooding toluene through the rock sample at different back-pressures. Figure 5.11 shows the calculated permeability for various pressure along with the calculated permeability range for the ambient pressure experiments. As a conclusion, no effect of the applied pressure range on the permeability was found.

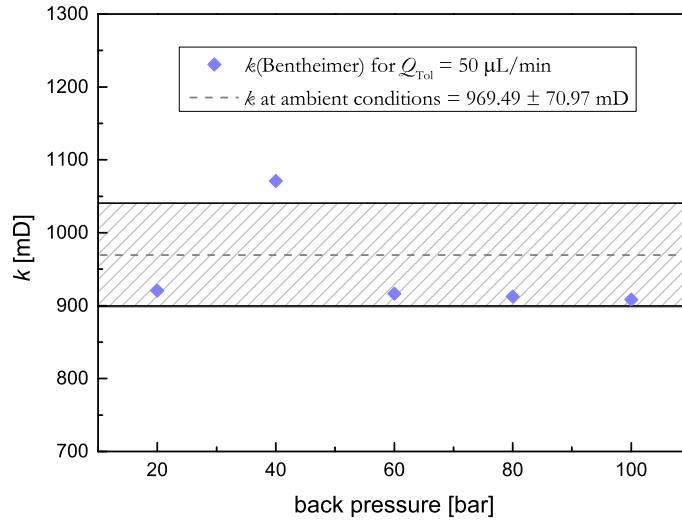


Figure 5.11: Permeability measurements at high pressure.

5.3.2 Porous Media Studies: Asphaltenes in Toluene and Heptane

Firstly, this sections discusses the shape of the pressure drop profiles, followed by showing example microCT scans of deposits to which LB calculations were applied to. Finally, a detailed application of the DBF model in terms of deposition profile and mechanism is presented.

5.3.2.1 Pressure Drop Measurements

Figure 5.12a and Figure 5.12b show the pressure drop history as a function of injected pore volumes (PV) in a semi-log graph at different flow rates. To compare the different flow rates, the pressure drop was normalised by subtracting the pressure drop at time $t = 0$ without deposition. The general trend is comparable to the capillary flow experiments: The pressure drop shows an increase at early times, indicating continuous deposition of asphaltenes. Eventually a steady state is reached,

suggesting a dynamic equilibrium between deposition and subsequent entrainment. The initial rate of pressure drop in Bentheimer seems to be identical in terms of PV, whereas the limiting pressure at steady state increases with flow rate, indicating more deposition.

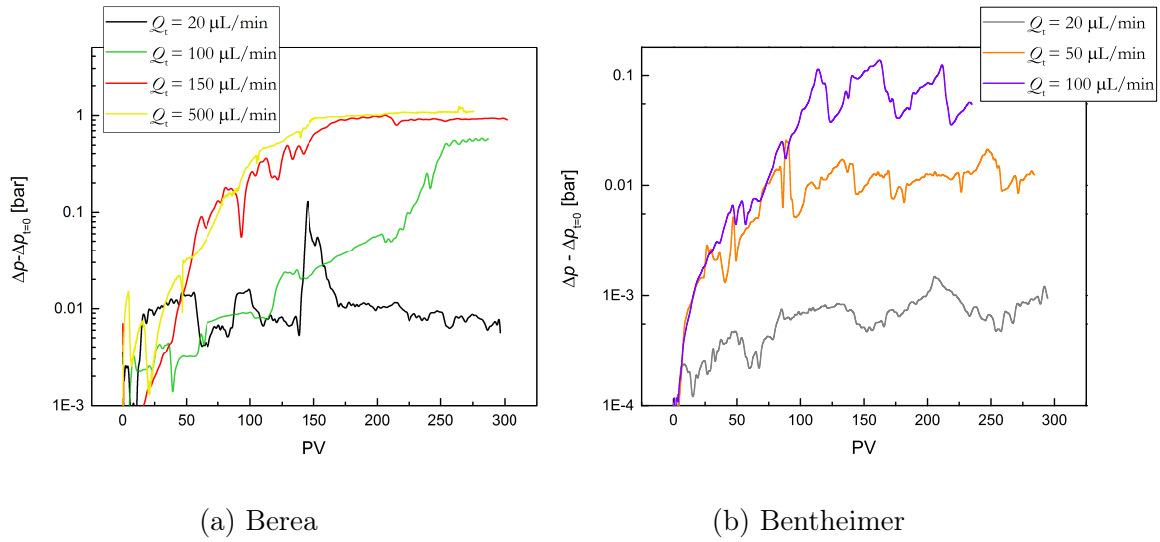


Figure 5.12: Pressure drop profile at various flow rates shown in a log-lin graph.

5.3.2.2 X-Ray Microtomography Imaging

The dry and wet samples were scanned with microCT to visualise deposited asphaltenes. Examples are shown in Figure 5.13 and Figure 5.14. The scans were taken after the core-flooding experiment in Bentheimer at a flow rate of $Q_t = 50 \mu\text{L}/\text{min}$. The filtered data were segmented into three phases by applying a watershed algorithm, shown in Figure 5.15. The segmented imaged was then used in Figure 5.16, which shows the volume rendering of an asphaltene deposit on the grain, where the pore phase was made invisible. The grains were rendered semi-transparent and the asphaltene floc in pink. Two volume rendered images are shown, obtained from two different subsections. Seemingly, asphaltene deposition does not lead to

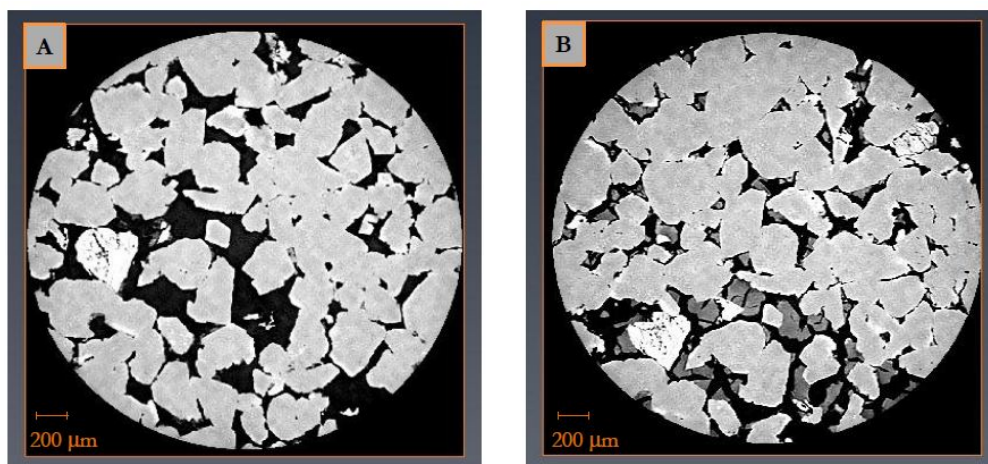


Figure 5.13: Comparison between a dry scan and a scan after deposition ($Q_t = 50 \mu\text{L}/\text{min}$) in Bentheimer. **A:** Dry scan with black pores and grey grains at a voxel resolution of $2.1 \mu\text{m}$. **B:** The same position was scanned after the experiment at the same voxel resolution, where the asphaltenes have a slightly darker grey scale compared to the grains.

a pore or pore throat blocking in the rock sample, instead the flocs coat the pore surface non-uniformly concentrated in particular patches.

Given the high concentration of asphaltenes in the core and to ensure a clear differentiation between surface deposition and possible deposition in a throat, more examples were analysed: To distinguish between pores and pore throats the “Separate Objects” module in Avizo was used, which applies a watershed line on a binarised image compared to the respective original one to compute a distance map. The shortest distance (indicative for pore throats) is highlighted. Each individual marker is showing a qualitative interpretation of a pore throat and was labelled automatically in different colours. 15 different sub-samples were analysed and a selection is presented in Figure F.2. 12 of them clearly showed that asphaltene flocs did deposit on the surface only (Figure F.2a - Figure F.2g), whereas some flocs deposited partially in a pore throat (Figure F.2g and Figure F.2h).

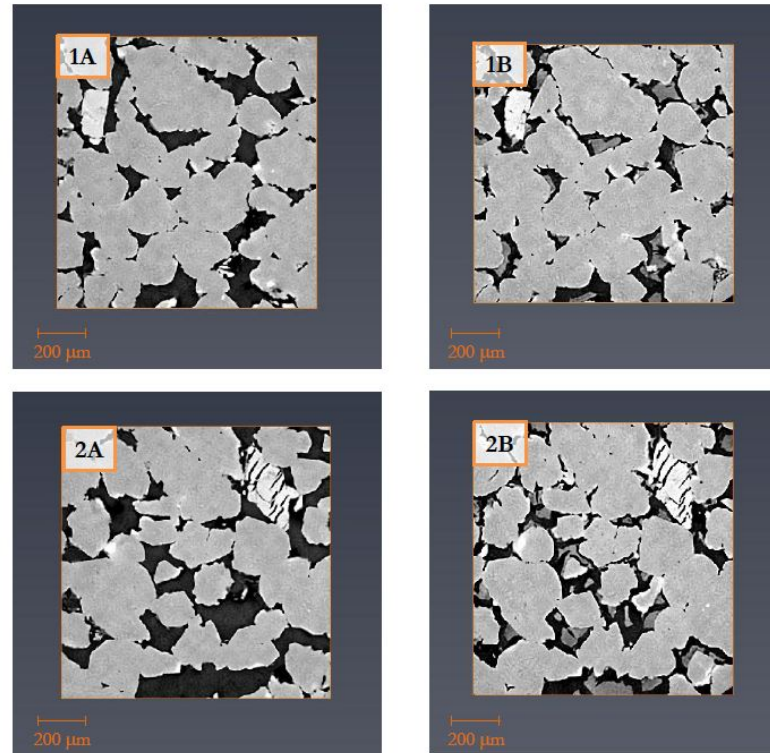


Figure 5.14: Comparison between a subsample of a dry scan and a scan after deposition ($Q_t = 50 \mu\text{L}/\text{min}$) in Bentheimer. **1A** and **2A**: Example of a dry scan, the two subsamples were taken from different slices. **1B** and **2B**: The same position was scanned after the experiment and shows the deposited asphaltenes in a different grey scale.

Due to the presence of clay, hence a more difficult segmentation, a different approach was taken to show asphaltene deposits in Berea. Figure 5.17 shows a dry scan and the same slice in the wet scan. The images were registered and then the dry images were subtracted from the wet scan. Theoretically, the remainders should only make asphaltenes visible, however as *in-situ* scanning was not possible, complete registration cannot be guaranteed and the first approach seems more promising at this experimental stage. Regardless, by looking at image B more blocking in the pore spaces seems evident than in Bentheimer, which would explain the drastic drop in permeability (discussed below).

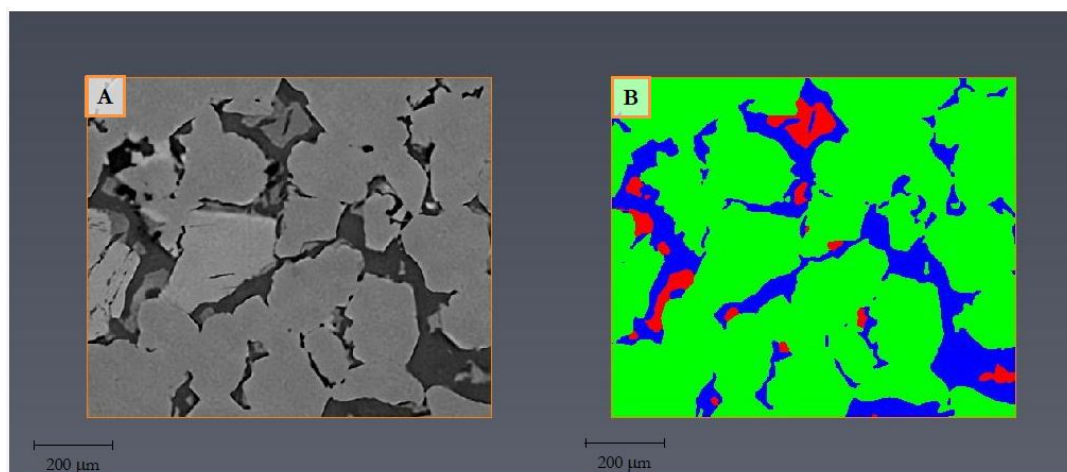


Figure 5.15: Example for a segmented subsection in Bentheimer after the deposition experiment ($Q_t = 50 \mu\text{L}/\text{min}$), scanned at a voxel resolution of $2.1 \mu\text{m}$. **A:** Filtered subsection of original raw image. **B:** Three phase segmentation; blue has been chosen for the pores, green represents the grains and red shows the deposited asphaltenes.

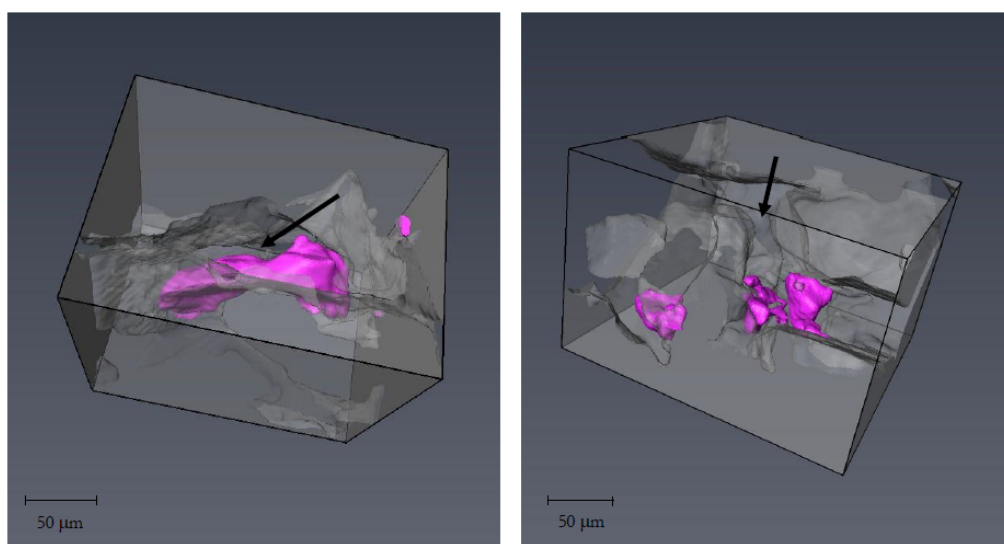


Figure 5.16: Volume rendering of an asphaltene floc (pink) deposited on the surface of a grain (grey). The direction of flow is indicated by the arrow.

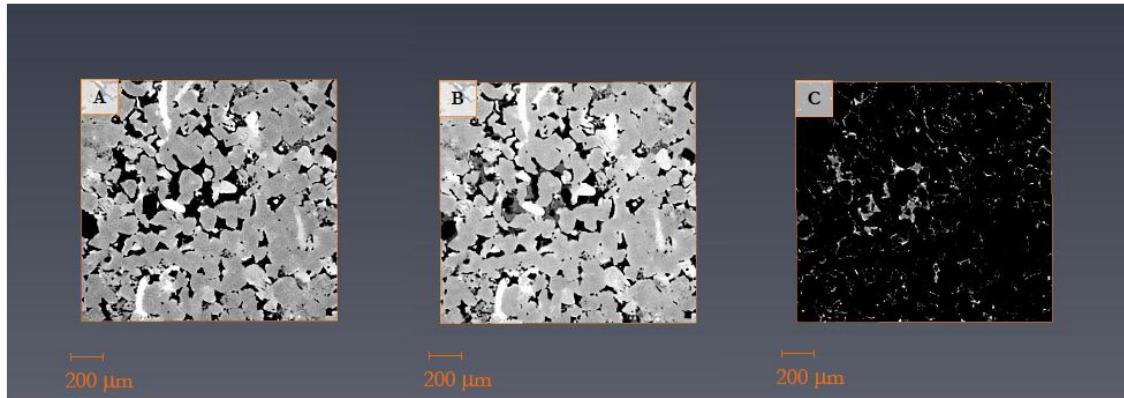


Figure 5.17: Registration of a wet scan (A) with reference to a dry scan (B) and the subtracted image (C) to show asphaltenes in Berea.

5.3.2.3 Permeability Calculations

Asphaltene deposition leads to severe permeability impairment, which can be assessed through pressure drop measurements and LB calculations from microCT images. The pressure drop at steady state was converted to permeability using Darcy's law ($k_{\text{exp.}}$). The permeability k_{LB} was calculated from microCT scans of Berea ($8.6 \mu\text{m}$) and Bentheimer ($2.1 \mu\text{m}$), with the region of interest being registered to the core inlet. The porosity $\phi_{\text{exp.}}$ and ϕ_{LB} for the wet samples are not shown here, as no satisfying data were obtained from the experimental weighing. The permeabilities k_{LB} , presented in Table 5.5, were only calculated for selected flow rates as it was not possible to scan the sample after every experiment conducted.

In all three examples $k_{\text{exp.}}$ is lower than k_{LB} , where the difference at the lower flow rates is within an acceptable order of magnitude. A significant discrepancy is observed, however, for Berea at higher flow rate; where the experimental permeability has dropped approximately 93% from the initial permeability. The deviations can possibly be attributed to the segmentation process, which is not straightforward due to the similar grey scale of asphaltenes, clay and grains; probably leading to an uncertainty in calculating k_{LB} . Only a small volume of the rock sample was scanned

and pore and throat plugging may have occurred towards the outlet of the core, thus leading to an underestimation by k_{LB} . As suspected from the pressure drop profiles, an increase in flow rate leads to a higher permeability impairment in Bentheimer. On the contrary, an increase from $Q_t = 150 \mu\text{L}/\text{min}$ to $500 \mu\text{L}/\text{min}$ in Berea leads to a slight permeability improvement, where the higher shear probably prevented further deposition.

Table 5.5: Experimental and theoretical permeabilities for Berea and Bentheimer at different flow rates.

	Flow rate [$\mu\text{L}/\text{min}$]	$k_{\text{exp.}}$ [mD]	k_{LB} [mD]
Berea	20	56.28	92.12
	100	26.99	/
	150	6.75	30.91
	500	16.30	/
Bentheimer	20	453.96	/
	50	208.04	319.58
	100	88.91	/

5.3.2.4 DBF Modelling

According to the images, asphaltenes rather deposit on the surface instead of plugging a pore throat. By comparing the pressure drop data to the DBF model, the damage due to deposition can be assessed further. The pressure drop data were converted into the dimensionless permeability k/k_0 (where, $k_0 = k_{0,\text{exp.}}$) and are shown along with the corresponding fit from the DBF model in Figure 5.18.

To obtain an acceptable match to the experimental data with the DBF model, the fitting parameters were tuned and optimised, shown in Table 5.6. The magnitude of the fitted parameters gives insight into the dominant mechanism of permeability impairment.

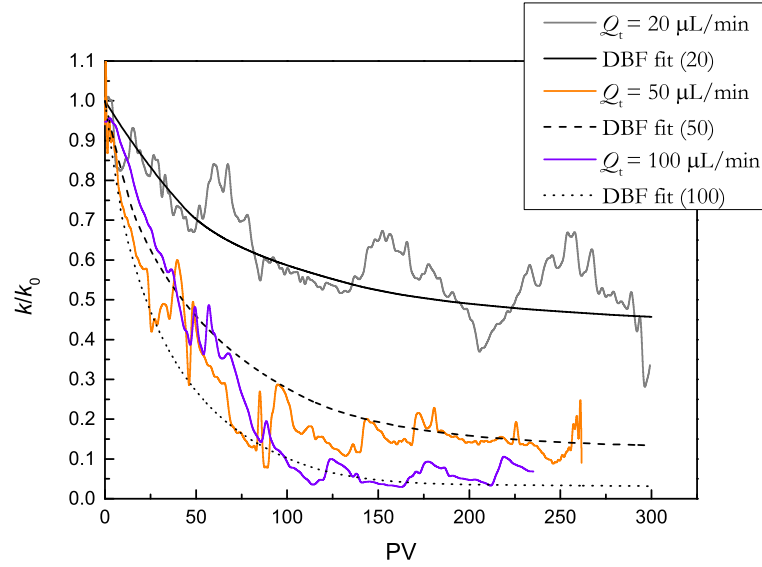


Figure 5.18: Dimensionless permeability k/k_0 as a function of injected PV in Bentheimer, comparing the experimental pressure drop data and the simulated DBF fit.

Table 5.6: Fitting parameters for the DBF model optimised to match the experimental data.

Parameter	Flow rate [$\mu\text{L}/\text{min}$]		
	20	50	100
$v_{L,cr}$ [cm/h]	1.2	4.5	14
α [1/h]	8.5	250	400
β [1/cm]	0.35	0.35	0.35
γ [1/cc]	0	0	0

Reduction in Permeability The best agreement was found by using the surface parameter α and the entrainment coefficient fitting parameters (β and $v_{L,cr}$). According to the simulated DBF fit, the damage during early time is dominated by surface deposition only, with an exponential decrease in permeability. The entrainment coefficients affect the fit after approximately 125 - 130 injected PV, showing a steady state condition with k/k_0 approaching a constant value.

Figure 5.19 highlights the entrainment process in grid cells 1 to 10 simulated for different experimental flow rates. The overall entrainment rate increases with increasing flow rate, which is due to more asphaltene deposition at early times ($=$ lower k/k_0). Therefore a higher entrainment rate is required at the higher flow rate to ensure the dynamic equilibrium. Similar to the capillary flow experiments, these data suggest that eventually a dynamic equilibrium between deposition and entrainment has been reached, where the experimental data are in good agreement when fitted with both parameters α and β .

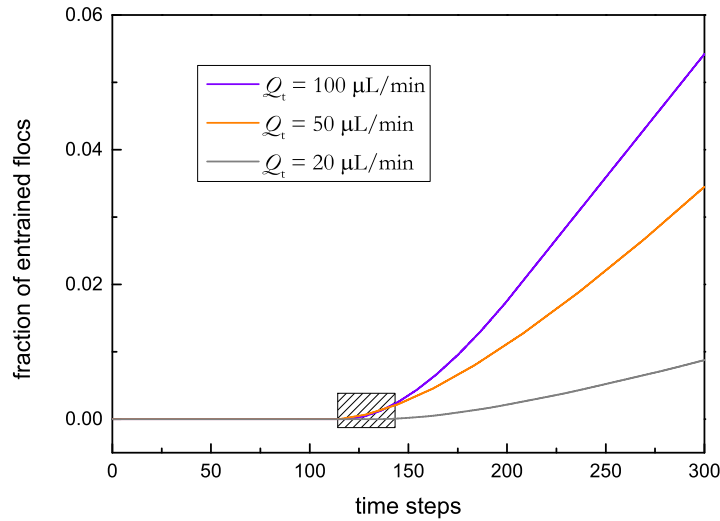


Figure 5.19: Effect of flow rate on the fraction of entrained flocs in Bentheimer using the DBF model. The initiation of entrainment seems to be independent of the three different flow rates simulated and starts at a range of 125 to 130 time steps.

The onset of entrainment is independent of the applied flow rate, also shown in Table 5.6, where a constant value of β provided the optimum fit. Establishing the force balance in Chapter 4 has shown that for entrainment the hydrodynamic forces need to be greater than the adhesion forces F_A . The higher flow rate results in a higher deposition rate due to smaller flocs experiencing faster diffusion to the

surface. For the smaller flocs a higher shear is subsequently required to initiate entrainment. Due to surface roughness caused by the deposit layer, the particle-to-surface distance increases, implying a smaller adhesion force. On the contrary, when a smaller floc fits into the roughness of the lumpy wall, F_A will be higher than theoretically expected based on the particle diameter. The balance between critical deposit layer thickness and $v_{L,cr}$ required for entrainment seems to result in independence of the flow rate.

Heterogeneous Deposition Profile In Chapter 4 it was hypothesized that asphaltene deposition may occur heterogeneously, as more deposits were found at the capillary inlet. Figure 5.20 shows the decrease in dimensionless permeability k/k_0 at two flow rates in cells 1 to 10 (injection to production well), which have previously been displayed in Figure 5.18. As a comparison, Figure 5.20 also shows the reduction in dimensionless permeability for cell 1 only, representing the fluid inlet in the corresponding experiment. The dashed and solid lines do not overlap, showing that in the simulation the damage across the length of the grid occurs heterogeneously. Near the injection point, entrainment starts earlier than towards the end of the simulation well, thus reaching the dynamic equilibrium at earlier time steps. The differences between asphaltene damage done in cell 1 compared to the overall grid length seem to be more pronounced at the lower flow rate, showing that the fraction of deposited flocs form a more uniform layer across cell 1-10 with higher flow rate.

The results corresponding to $Q_t = 100 \mu\text{L}/\text{min}$ were further analysed in terms of the position in the simulation grid in the direction of flow (Figure 5.21). The volume fraction of surface deposited asphaltenes E_α (without considering entrainment effects) in cells 1-10 is shown here for various time steps, with the lowest one being near the simulation start and the time step = 300 corresponding to the end

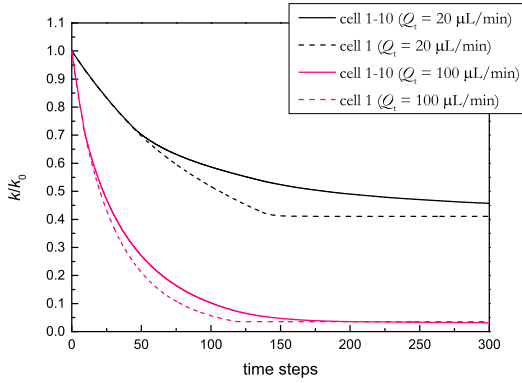


Figure 5.20: Dimensionless permeability k/k_0 in Bentheimer as a function of simulation time steps comparing the asphaltene damage for cell 1 and cells 1-10 at two different flow rates ($Q_t = 20 \mu\text{L}/\text{min}$ and $100 \mu\text{L}/\text{min}$).

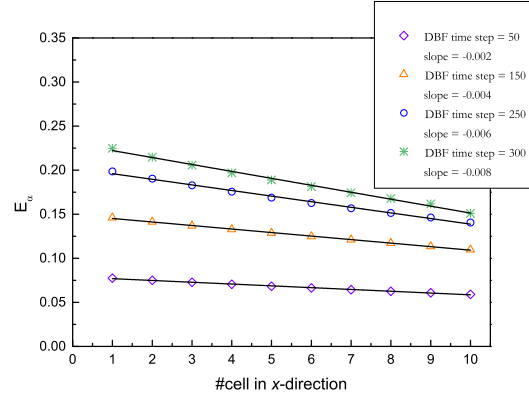


Figure 5.21: Heterogeneous surface deposition profile with increasing number of grid cells at various simulation time steps ($Q_t = 100 \mu\text{L}/\text{min}$).

of the simulation. At a given time step, more asphaltenes deposit near the inlet; a trend which is evident for all time steps. Further, the steeper slope indicates that the non-uniformity becomes more pronounced with progressing time.

In addition, microCT images and LB calculations were used to confirm the results shown in the DBF simulations. Figure 5.22 shows a 3D volume rendered image of a subsection of Berea (voxel resolution = $8.6 \mu\text{m}$). For clarity purposes only pore space is displayed. This image is used here to represent the topographies of a wet scan ($Q_t = 100 \mu\text{L}/\text{min}$). Different sections across the length of the rock sample were scanned from bottom to top. The yellow lines (A to C) show the subsections scanned at a voxel size of $8.6 \mu\text{m}$ and the red ones (1 to 3) the subsections scanned at $2.2 \mu\text{m}$ voxel resolution, where A and 1 indicate the fluid inlet. Figure 5.23 shows the calculated dimensionless k_{LB} for the different sections across the actual length of the rock sample. At both voxel resolutions, the dimensionless permeability increases with increasing distance from the rock core inlet.

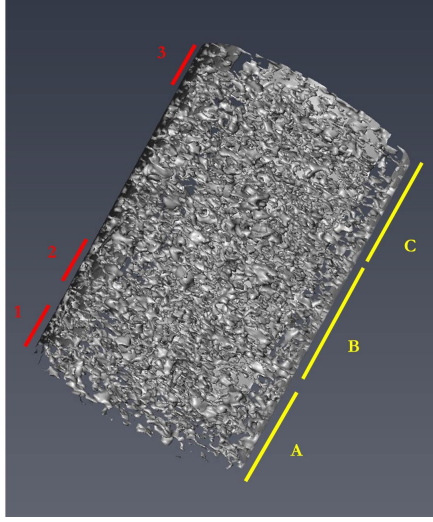


Figure 5.22: Volume rendered image of pore and pore throats in Berea.

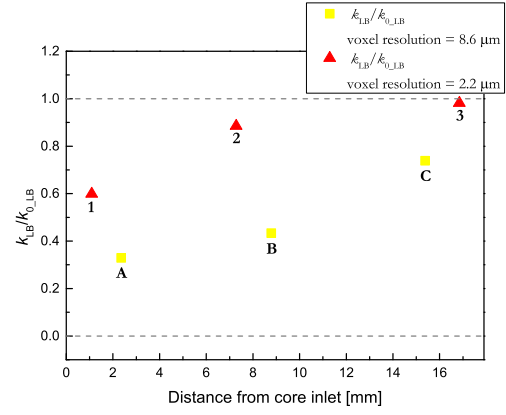


Figure 5.23: Change in dimensionless permeability in Berea at two different voxel resolution with increasing distance from the core inlet.

From both DBF (Bentheimer) and the combination of microCT+LB (Berea), it can be concluded that deposition occurs heterogeneously along the length of the sample and from the DBF model, that injecting the suspension at a higher volumetric flow rate leads to a more homogeneous deposit layer along the core sample, which is in agreement with the capillary flow experiments.

Berea vs. Bentheimer Both sandstones have a different initial permeability k_0 , with the Berea exhibiting a much smaller one. By comparing the pressure drop data at the same experimental conditions to the DBF model with the same boundary conditions (Figure 5.24), the effect on permeability impairment is discussed here.

Due to smaller pores and pore throats in Berea, surface deposition causes more damage at early times, as seen in the sharper drop in permeability. Therefore, the critical interstitial velocity $v_{L,cr}$ is reached earlier and the deposited flocs get entrained in the flow. As asphaltenes are a polar component, interactions with

components such as clay may lead to stronger interaction among the rock surface and the asphaltenes, thus increasing the amount of asphaltene deposition during early injection. Even though the equilibrium between surface deposition and entrainment is reached earlier in Berea, the final impairment due to asphaltene deposition seems to be independent of the initial permeability.

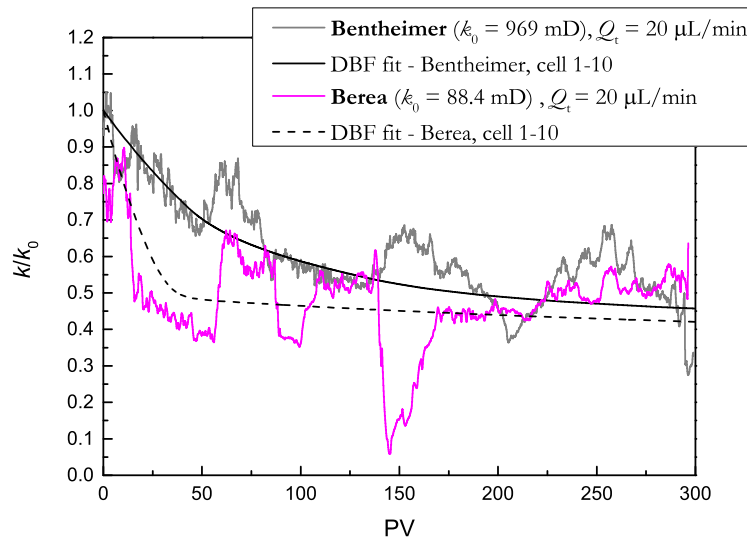


Figure 5.24: Change in dimensionless permeability in Berea and Bentheimer including the corresponding DBF fit.

5.3.3 Porous Media Studies: Diluted Crude Oil and CO₂

The following section is structured similarly to the previous one: Firstly, the pressure drop profiles are presented which are followed by example microCT images of asphaltene deposits. The section then concludes by comparing the DBF fit to the dimensionless permeability, particularly focusing on the deposition mechanism.

5.3.3.1 Pressure Drop Measurements

The diluted crude oil was co-injected with CO₂ through Bentheimer at $T = 323$ K, whilst simultaneously recording the pressure drop. To ensure reproducibility, repeat experiments were carried out. Two different system pressures were tested, shown in Figure 5.25a and Figure 5.25b. No significant pressure drop was detected at a back-pressure of 140 bar and a flow rate of $Q_{\text{oil}} = 0.05$ mL/min. A doubling in flow rate showed a small and gradual increase in pressure drop with more injected PV. MicroCT images are presented below to discuss whether the increase in pressure drop can be attributed to asphaltene deposition. Next, the system pressure was set to $p = 150$ bar, resulting in a much steeper increase in pressure drop at the low flow rate. According to the solubility measurements (Chapter 3), the pressure chosen should be sufficient to ensure that the mass fraction of dissolved CO₂ is above the precipitation onset point, despite the high uncertainties in the solubility measurement.

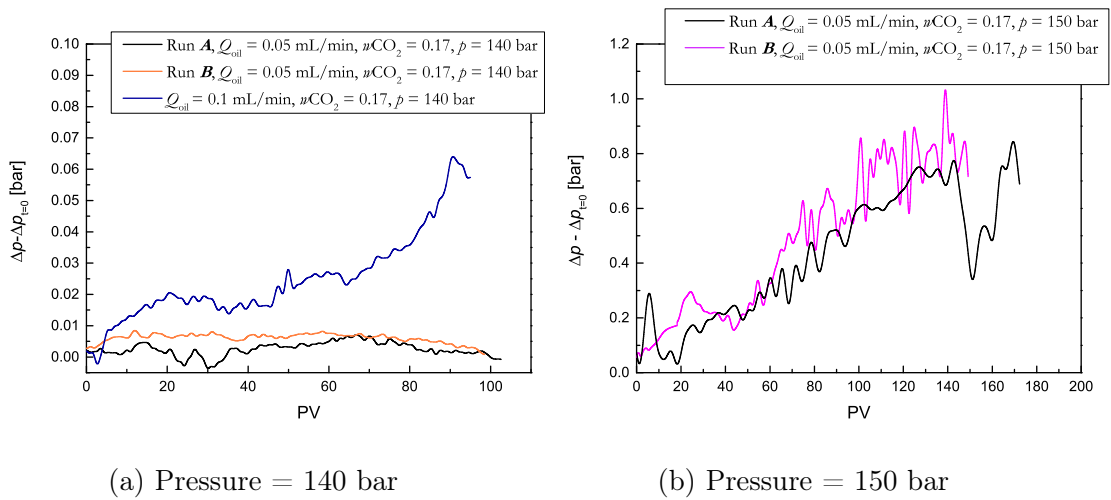


Figure 5.25: Pressure drop profile at different system pressure and flow rates as a function of PV.

5.3.3.2 X-Ray Microtomography Imaging

The scans shown in Figure 5.26 were taken after Run *B* at $p = 150$ bar (1B and 2B) and $Q_{\text{oil}} = 0.1$ mL/min at $p = 140$ bar (1A and 2A). The two latter ones do not show any deposits in the pores, even though an increase in pressure drop was measured. The change in pressure drop probably occurred due to phase separation or incomplete mixing of the components. Even though the filtration and solubility measurements were at equilibrium at $p = 140$ bar, the time scale in the core-flooding experiments was too short to fully saturate the oil and to lead to visible deposition.

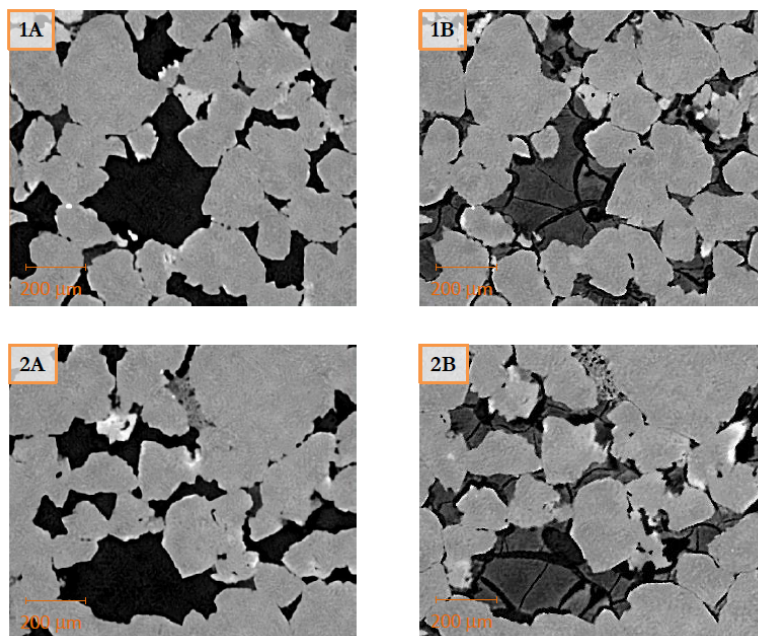


Figure 5.26: Scanned sub-volumes (voxel resolution = $2.1 \mu\text{m}$) for two CO_2 experiments at different pressures. **1A** and **2A**: No visible asphaltene deposition from the experiment at $p = 140$ bar with $Q_{\text{oil}} = 0.1$ mL/min can be observed. **1B** and **2B**: The same position now showing deposits at $p = 150$ bar (Run *B*).

The scans 1B and 2B show deposits, where seemingly the increase in pressure was sufficient to initiate asphaltene precipitation and deposition. CO_2 caused the asphaltenes to swell in the pores, which then cracked once the experiment was

depressurised. When compared to heptane induced precipitation and deposition, more asphaltenes deposit in the pores and pore throats, which is further highlighted in Figure 5.27. This image shows a volume rendered image of an asphaltene floc plugging a pore throat. Further examples are shown in Figure F.1, where the pore throats are marked in different colours. 9 different sub-samples were compared, in which 8 of them showed deposition in both pore and pore throats (Figure F.1a - Figure F.1c), whereas one example shows that asphaltene deposition occurred in the pores only, leaving the throat unobstructed (Figure F.1d).

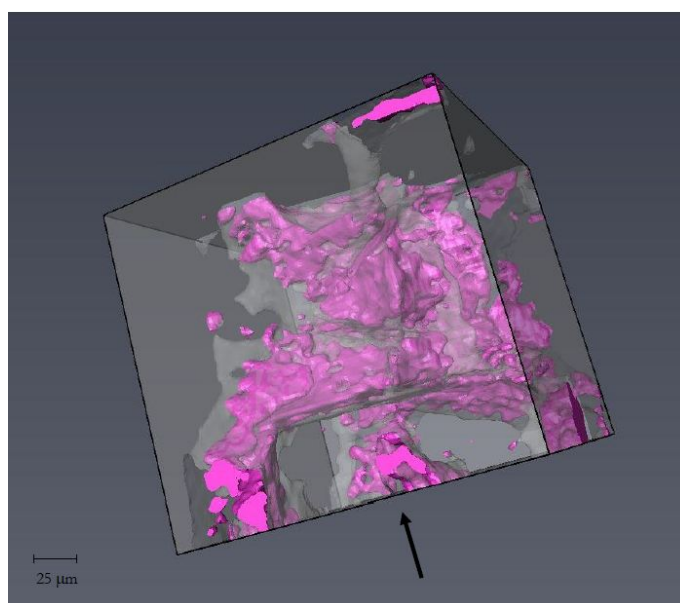


Figure 5.27: Volume rendering of an asphaltene floc (pink) plugging a pore throat (grey). The direction of flow is indicated by the arrow.

Once particles have deposited in the pore throats, they may form bridges while still allowing for fluid to pass through. Fluid seepage, however, only occurs if the particles do not fully seal the throats. The approaching fluid in the suspension flows through the throats, while filtering out the asphaltenes, hence forming an internal filter cake in the adjoining pores. The high fraction of deposited asphaltenes in the pores is therefore likely due to the retention of particles accumulating behind the

throats.

5.3.3.3 Permeability Calculations

The permeability was converted from the pressure drop using Darcy's law and then compared to the LB calculations (Run *B* at $p = 150$ bar (Table 5.7)). Similar to the permeability calculations at the ambient experiments, $k_{\text{exp.}}$ is smaller than k_{LB} . As only a small sub-sample of the rock core was scanned, this difference is within an acceptable order of magnitude.

Table 5.7: Permeability in Bentheimer determined experimentally and through simulation at $p = 150$ bar and $Q_{\text{oil}} = 0.05$ mL/min (Run *B*).

	Oil flow rate	$k_{\text{exp.}}$	k_{LB}
	[$\mu\text{L}/\text{min}$]	[mD]	[mD]
Bentheimer	50	77.02	96.72

5.3.3.4 DBF Modelling

One example pressure drop profile was converted into the dimensionless permeability, which then the DBF model was fitted to. The DBF model was adjusted according to the experimental conditions and is shown in Figure 5.28. The transient pressure drop data were fitted by using the surface deposition parameter α , the plugging parameter γ and after approximately 75 time steps a dynamic equilibrium between entrainment (by taking into account β) and further deposition can be observed, as the dimensionless permeability levels off. The optimised parameters are displayed in the graph below.

According to Figure 5.28 three different formation damage regions can be identified. **Stage 1:** During the initial stages of the suspension flow through the rock sample the flocs deposit on the surface of the pores. The surface deposition leads to the most significant permeability impairment in the form of an exponential decrease.

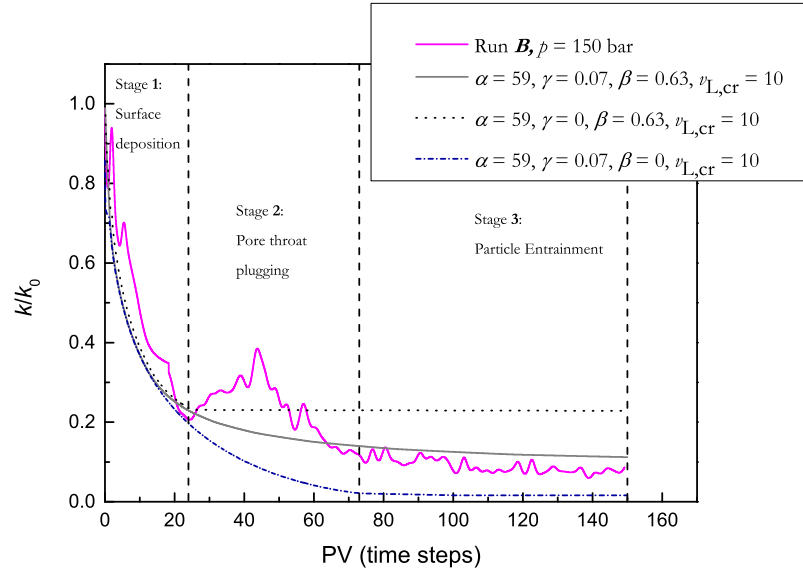


Figure 5.28: Permeability impairment experimental data along with fitted DBF model for one CO₂ experiment (Run *B*, $p = 150$ bar).

Stage 2: At the beginning of that region a slight permeability improvement by entrainment is seen. After approximately 43 injected PV, the permeability declines more dramatically than in the previous region in a linear way. This drastic change can probably be attributed to pore throat plugging. **Stage 3:** The counter effect of deposition and entrainment results in a steady state condition so that the permeability reaches a constant value. At steady state the rate of deposition is almost equal to the rate of entrainment.

In this case, the DBF model does not seem to represent the experimental data sufficiently. The steep drop due to possible plugging is not captured entirely and the model does not distinguish whether entrainment occurs due to pore surface entrainment or due to a counter-mechanism of pore throat plugging: A partial re-opening of the plugged pores. This mechanism is further discussed below.

Additionally, Figure 5.28 shows that the experimental data cannot satisfactorily be matched, if either γ or β are switched off. In this particular example the

permeability impairment can most efficiently be captured as described above.

5.3.4 Limitations and Modification of the DBF Model

The DBF model fitted to the pressure drop data supports the results qualitatively very well when compared to the microCT images. Satisfactory agreement was also found by reproducing a data set by Minssieux (1997). However, the change in deposition rate due to variations in shear was not sufficiently experimentally studied in the literature and hence no comparable simulations were obtained. Modified rate equations are necessary to account for surface roughness, non-uniformity of pores and pore throats and effect of wettability. Further, considering particle properties such as size distribution, deformation, sticking probability and variations in the concentrations profiles play a crucial role in understanding asphaltene deposition. Describing the rate equations at a macroscopic level though, allows for some reasonable justifications. Limitations in the model arise due to unavailability of sufficient experimental data. The findings obtained in this work will be used to capture some of the features mentioned and propose some improvements to the current model. Separating the net deposition into four sub rate equations allows for a better understanding of each mechanism leading to asphaltene damage.

However, the biggest drawback in the model at its current state will always be that choosing and optimising the fitting parameters will remain an empirical process, which can then be used to interpret the experimental data. The rate equations are therefore not workable in a predictive way as the parameters cannot be estimated by any other mechanism than fitting them to the experiments. Therefore, the rate equations established should be treated with caution as, even though an improved description an understanding will be achieved, more complications, such as more fitting parameters are introduced.

Surface Deposition Rate Equation The first rate equation, describing the pore surface deposition, does not account for a higher deposition rate with smaller floc size. As seen in the DLS measurements (Chapter 4), the floc size decreases with increasing shear within the experimental conditions studied. Smaller flocs experience faster diffusion to the surface, resulting in more deposits at steady pressure. According to Reuvers and Golombok (2009), the flow rate is related to the shear rate $\dot{\gamma}$ in a porous medium in the following expression:

$$\dot{\gamma} = \frac{v}{\sqrt{k}} \quad (5.8)$$

where, v = interstitial velocity = u/ϕ ; u = superficial velocity = Q_t/A ; A = cross sectional area

By considering the dependence of deposition and particle size on shear rate, a critical shear rate ($\dot{\gamma}_{cr}$) can be defined. At low shear, a depletion of particles able to deposit is caused by the particle growth due to aggregation. Near a no-slip surface, a diffusive boundary layer will be present in the flow. However, if the boundary layer is smaller or equal to the size of the particles, meaning that the diffusive layer would end at the size of the particle, no asphaltenes are being deposited. Therefore, below the critical shear rate, the availability of particles able to deposit is limited. The critical shear rate depends on the stickiness of the particles and the particle size, which can be approximated through the adhesion force F_A , described in the previous chapter:

$$F_A = \frac{H a_p}{12 z_0^2} \quad (5.9)$$

where, H = Hamaker constant; z_0^2 = distance of minimum approach between particle and surface

The critical shear rate is then given by:

$$\dot{\gamma}_{\text{cr}} = \frac{\tau_{\text{cr}}}{\mu}$$

with

$$\tau_{\text{cr}} = \frac{F_A}{A_\phi}$$
(5.10)

where, τ_{cr} = critical shear stress; μ = dynamic viscosity of the fluid mixture; A_ϕ = pore surface exposed to flowing fluid, which can be approximated by $\approx \phi^{2/3}$

To understand the relationship between the surface deposition of asphaltenes in the core-flooding experiments and the applied shear rate, the volume fraction of surface deposited asphaltenes, previously shown in Figure 5.18, is plotted as a function of simulation time steps.

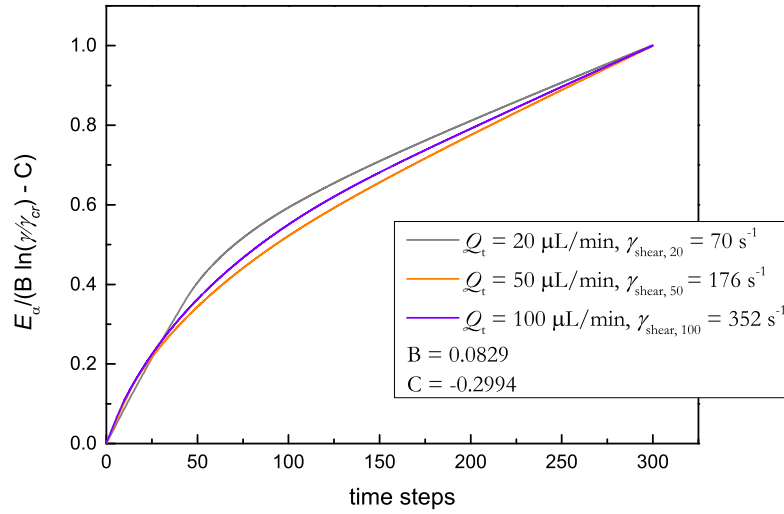


Figure 5.29: Volume fraction of deposited asphaltenes on the pore surface (E_α) normalised by the applied shear rate, simulated with the DBF model. The amount of deposited particles is proportional to $\ln(\dot{\gamma}/\dot{\gamma}_{\text{cr}})$.

The fraction of surface deposited asphaltenes at the different shear rates can

therefore be expressed with:

$$E_\alpha = B \ln \left(\frac{\dot{\gamma}}{\dot{\gamma}_{cr}} \right) - C \quad (5.11)$$

where, B and C = empirical constants

The pore surface deposition rate with regards to the shear rate is then is given by:

$$\begin{aligned} \frac{\partial E_\alpha}{\partial t} &\cong \alpha \ln \left(\frac{\dot{\gamma}}{\dot{\gamma}_{cr}} \right)^n \\ \alpha &= \alpha_i, \text{ when } \dot{\gamma} > \dot{\gamma}_{cr} \\ \alpha &= 0, \text{ when otherise} \end{aligned} \quad (5.12)$$

where, n = exponent describing the degree of intensity of $\dot{\gamma}$ on E_α

The assumption that the volume fraction of asphaltenes in the suspension C_A is the same in pore and pore throats may not be reasonable as they are not uniform and rather represented by a size distribution. The pore and throat sizes also vary during deposition and removal. Instead of considering C_A only, E_α can be described proportionally to the diffusive flux j . The diffusive flux in terms of volume fraction is described as:

$$j = -D \frac{\partial(\phi \rho_p C_A)}{\partial y} \quad (5.13)$$

where, D = diffusion coefficient; y = distance normal to the surface

Applying Equation (5.13) in Equation (5.1) yields the pore surface particle deposition rate equation with regards to the diffusive flux:

$$\frac{\partial E_\alpha}{\partial t} \cong \alpha - \left(D \frac{\partial(\phi \rho_p C_A)}{\partial y} \right)^l \quad (5.14)$$

where, l = exponent describing the degree of intensity of j on E_α

Pore Surface Particle Entrainment In the previous chapter a force balance was established, saying that for particle entrainment the hydrodynamic forces F_H , acting on the attached particles, need to be greater than the adhesion forces F_A . As ideally the force balance should be described in a dimensionless way, the approach of the critical particle Reynolds number $Re_{p,cr}$ can be used. Re_p provides a means for scaling the requirement for detachment to particle diameter and fluid flow conditions. Substituting the definition for the particle Reynolds number into the force balance equation, the removal criteria can be expressed as:

$$Re_p \geq \frac{-F_A C_A}{1.7 \times 3\pi} \left(\frac{\rho}{\mu^2} \right) \quad (5.15)$$

Re_p is defined as:

$$Re_p = \frac{\rho_p C_A v a_p}{\mu} \quad (5.16)$$

where, v = velocity of the particles which can be approximated to the velocity of the flowing suspension while neglecting slip; ρ_p = particle density

In general, removal will occur when:

$$Re_p(\text{flow}) \geq Re_{p,cr} \quad (5.17)$$

Below the critical value, the particles will remain attached to the wall. Critical

particle diameters can be determined for which the removal forces are larger than the attractive forces between particle and surface. However, real systems are determined by rough and deformable particles with a wide size distribution being deposited on a lumpy surface. This results in multiple ranges of adhesion forces.

To describe the rate equation for entrainment, the fitting parameter β should not only depend on the critical interstitial velocity. The force balance acting on the particle in terms of Re_p should be considered instead.

Pore Throat Plugging The results shown in Figure 5.28 and Figure F.1 have shown pore surface and pore throat deposition. The particles gradually build up at the pore throat, thus reducing its diameter. This process continues until the throat is obstructed by bridging (Gruesbeck and Collins 1982). That phenomenon was further described by Tran et al. (2009), who introduced a pore throat-to-particle diameter ϵ . The gradual build up will therefore continue as long as ϵ is greater than a critical value ϵ_{cr} . If $\epsilon \leq \epsilon_{cr}$, then the throat is fully obstructed and the particles deposit in the pores behind the plugged throats.

By considering that event, the pore-filling rate constant Γ is introduced into the rate equation:

$$\frac{\partial E_\gamma}{\partial t} \cong \Gamma + \gamma \phi C_A \left[\frac{1}{\epsilon} - \frac{1}{\epsilon_{cr}} \right] \quad (5.18)$$

$$\Gamma = 0, \text{ when } \epsilon \geq \epsilon_{cr}$$

Pore Throat Opening The mechanism, described by Kord et al. (2014), introduces the counter effect to pore throat plugging: The pore throat opening, which might be responsible for the steady permeability at more injected PV. Due to plugging, the velocity increases which can release some of the jammed particles in the throats, thus resulting in a partial throat opening and providing less restricted flow pathways. This mechanism can be introduced into the net deposition rate equa-

tion by defining another critical interstitial velocity above which removal from the throats occurs.

5.4 Chapter Conclusions

Core-flooding experiments were conducted to investigate the effect of asphaltene deposition on permeability in a real sandstone reservoir rock. Pressure drop measurements and combined microCT imaging and lattice-Boltzmann calculations have shown a decrease in permeability with more asphaltenes being deposited at higher flow rate. The impairment model by Wang (2000) and Wang and Civan (2001) has successfully been validated against the experimental results.

Surface deposition is the dominant mechanism of formation damage when heptane precipitated asphaltenes deposit in the rock core at ambient conditions. The permeability continues to decrease until a counterbalancing mechanism of entrainment comes into effect. CO₂-asphaltenes exhibit a different particle-wall interaction and surface deposition is followed by partial plugging of the pore throats. The particle deposition on the pore surface seems to be the main reason for permeability impairment in the way that it decreases exponentially with injected PV. It occurs during early stages of injected PV and imposes a permeability impairment in the range of 50 to 80% reduction compared to the initial permeability.

The DBF model at its current states fails to distinguish whether subsequent permeability improvement can be attributed to pore surface entrainment or pore throat opening. Some important revisions about the DBF model were presented at the end of the chapter.

Chapter 6

Conclusions and Future Work

Hydrocarbons belong to the most intricate fluids on earth; a crude oil may be comprised of more than 20,000 chemical components, in which asphaltenes are the heaviest and most complex substances. It is therefore not surprising that even after decades of intensive asphaltene research, controversy still exists about their molecular structure, molar mass and the mechanisms leading to self-association, precipitation and deposition. The way forward in asphaltene science relies on further investigation of the fundamentals behind these components. This thesis presented an insight into crude oil asphaltene precipitation and subsequent deposition induced by both hydrocarbons and CO₂, contributing to closing literature and research gaps.

Throughout this thesis, experimental and computational techniques have been applied to reconcile asphaltene precipitation in terms of the definition of asphaltenes as a “solubility class” at both ambient and reservoir conditions. Understanding precipitation is a first step towards a solution dealing with one of the major asphaltene related challenges in the petroleum upstream industry; their deposition in the pores and pore throats of reservoir rocks. Asphaltene deposition was studied in different geometries ranging from a simple capillary to a cylindrical rock core. The conclusions and recommendations for future work are presented here in Section 6.1 and

Section 6.2, respectively.

6.1 Conclusions

Asphaltene precipitation from a Zuata heavy crude oil (C7-asphaltene content: 16.1wt%) was investigated through **filtration experiments**, on addition of *n*-alkane solvents to a diluted crude oil at ambient conditions and compared to CO₂ induced precipitation under elevated condition at $T = 323$ K and within a pressure range from 1 to 220 bar. For pure alkanes, the amount of asphaltenes precipitated beyond the onset point increased linearly with the mixture solubility parameter with a common precipitation onset point ($\delta_{\text{onset}} = (16.45 \pm 0.13) \text{ MPa}^{0.5}$). For the first time, hydrocarbon precipitation experiments have been thoroughly compared to CO₂ precipitation experiments and combined with an estimated mass of CO₂ dissolved in crude oil, where the assumption of full miscibility is no longer valid. The results have demonstrated that CO₂ follows the same behaviour when the precipitation onset point is described in terms of the mixture solubility parameter. The here described approach is capable of predicting the onset point and the maximum amount of precipitated asphaltenes for a given precipitant at varying pressure conditions.

These findings were then used to choose appropriate flow regimes and experimental conditions in subsequent deposition studies.

Asphaltene deposition was studied in **capillary flow** and **core-flooding** experiments. In the capillary flow experiments asphaltenes were precipitated with heptane from a toluene diluted crude oil at ambient conditions. The same system was subsequently studied in core-flooding experiments and then extended to CO₂ induced precipitation at $T = 323$ K and pressures of 140 and 150 bar. Deposition was assessed through pressure drop measurements and successfully compared to multiscale

computer simulations.

Existing capillary flow studies in the literature were improved by not only attributing pressure drop measurements to deposition, but extending the analysis to imaging the deposits, precise mass measurements and particle size analysis, revealing that higher pressure drop does not necessarily correspond more deposit build up. Images at steady pressure revealed a non-uniform deposition profile, with more deposits build up at the fluid inlet stream, most likely being caused by transport limitations of asphaltene flocs diffusing to the surface. With higher shear, by increasing the flow rate from 10 to 80 $\mu\text{L}/\text{min}$, the deposition profile across the capillary length became, however, more homogeneously. The mass of deposits was measured from 2 to 80 $\mu\text{L}/\text{min}$ and it was found that an increase in deposition with higher flow rates is thought to occur due to a balance between adhesion and hydrodynamic forces acting on the attached particles, such that smaller particles deposit on the surface more easily. The deposit layer continued to grow as long as the forces among the particles and between the particles and the surface were greater than shear removal forces. At a particular deposit thickness, the hydrodynamics outweigh adhesion and the growth of the deposit layer is limited, resulting in a dynamic equilibrium between deposition and entrainment. This interplay of forces resulted in the interesting observation that both the pressure drop in the capillary and the mass of asphaltenes deposited increased linearly with the square-root of the volumetric flow rate, showing a behaviour which has not previously been illustrated in the literature.

Studies in a porous medium (Bentheimer and Berea sandstone) allowed for further distinction between pore surface and pore throat deposition. On the basis of pressure drop measurements and an incorporated deposition model, the following conclusions were drawn: During early stages of fluid injection a rapid drop within 50 to 80% in permeability was encountered, associated with surface deposition which was found to be the main mechanism of asphaltene damage, where the results show a

very good match between experimental data and the deposition model. Even though the precipitation onset point was not affected by the precipitant, the mechanism contributing to asphaltene damage varied between the heptane and CO₂ experiments. Partial pore throat plugging was observed for the CO₂-asphaltenes, also causing a particle build up in the adjoining pores. This could be due to a difference of particle-particle and particle-wall interaction forces between the two precipitants. The data were further supported by microCT images, clearly revealing asphaltene deposits in pores and pore throats in high resolution, thereby providing a fundamental understanding of asphaltene deposition regimes in porous medium.

6.2 Recommendations for Future Work

The Interaction Potential The SRD simulations have shown that, by varying the well depth ε in the screened Coulomb potential, the interaction among the colloids can be changed; with increasing well depth, the asphaltenes became “stickier”, eventually leading to transient or complete blocking of the capillary.

Experimentally investigating the interaction force between asphaltenes-asphaltenes and between asphaltenes-surfaces could also reveal information about the deposition rate and forces dominating adhesion and removal. Knowing the interaction between asphaltenes and a rock surface could be incorporated into the DBF model, enabling it to be used in a more predictive way. The critical interstitial velocity, above which entrainment occurs, can be related to the magnitude of the interaction force as in the current model that parameter is simply assumed to be a constant.

Atomic Force Microscopy (AFM) is a widely applied technique to measure the interaction force at the atomic or nanoscale level. Asphaltene interactions can be measured in different solvent environments, hence assessing the solvent quality in terms of the ability to stabilise asphaltenes. The change from repulsive forces in

a “good” solvent to attractive v.d.W. forces in a “poor” solvent can be captured, thus quantifying the effect of any precipitant. Estimating the interaction force in a heptane or CO₂ environment will help to evaluate the different deposition mechanism observed in the porous media studies.

In-Situ Scanning Image acquisition of the asphaltenes in the rock cores was only done at a ambient pressure before and after the deposition experiment due to equipment limitations. This could have introduced artefacts during de-pressurisation and also precluded obtaining images at different stages during the deposition process for comparison to the transient pressure data.

X-Ray Microtomography can also be applied to conduct *in-situ* scanning of the asphaltene deposition and entrainment process in the rock cores as a function of injected volume. The continuously obtained scans could then simultaneously be compared to pressure drop measurements. A key requirement for the adapted experimental set-up is for the core holder to remain sufficiently X-Ray transparent to allow for imaging. A suitable material could be a Hassler type flow cell built around a carbon fibre sleeve. The cell, however, would have to be custom designed, similar to the design presented here (Section 5.2.2), as the requirement for co-injecting the fluids is stringent to avoid deposition in the flow lines. Additionally, the core holder has to withstand the described temperature and pressure; previous work has shown that the required conditions can be met (Andrew et al. 2014; Singh et al. 2016). In this work, the polyetherketone (PEEK) lines had to be changed to rigid metal lines as they were not compatible with the crude oil+CO₂ mixture, which can lead to an experimental shortcoming during scanning. As the core holder will be mounted inside the microCT and rotated relative to the pumps, the flow lines also need to be rotated. Metal flow lines can cause sample movement, thus reducing image resolution and make the data set unusable as subsequent image registration will not be

possible. To prevent this, flexible tubing should be used, where a replacement for PEEK and metal lines could be polytetrafluoroethylene (PTFE). The compatibility with crude oil and to ensure that no CO₂ diffuses through the lines within the required time period should be tested beforehand.

As a recommendation, this project should then be dedicated to the majority of a PhD thesis as the cost for a custom designed core holder ranges between £20,000 - 30,000 (private correspondence).

Chemical Characterisation of Asphaltenes The advantage of filtration experiments is that asphaltenes are being physically extracted and separated from the crude oil, thus allowing for further characterisation in terms of their chemical composition. Possible analytical techniques are mass spectrometry or ¹H or ¹³C nuclear magnetic resonance (NMR) spectrometry. Therefore it can be further distinguished between the structure of C7 and CO₂-asphaltenes, thus clarifying their effect on deposition discussed in this work.

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Appendix A

Filtration Experiments and Solubility Parameter

A.1 The Solubility Parameter δ_i for Pure Components

A.1.1 $T = 298\text{ K}$

Table A.1: Measured n and calculated values of F_n and δ for crude oil.

Crude oil	n	F_n	δ_i [MPa ^{0.5}]
1	1.5695	0.32786	19.96
2	1.5695	0.32786	19.96
3	1.5696	0.32790	19.96
Mean value	1.5695	0.32786	19.96

Table A.2: Measured n and calculated values of F_n and δ for toluene.

Toluene	n	F_n	δ_i [MPa ^{0.5}]
1	1.4969	0.29257	18.13
2	1.4968	0.29252	18.13
3	1.4969	0.29257	18.13
Mean value	1.4969	0.29255	18.13

Table A.3: Measured n and calculated values of F_n and δ for n -heptane.

n-heptane	n	F_n	δ_i [MPa ^{0.5}]
1	1.3889	0.23646	15.21
2	1.3887	0.23635	15.20
3	1.3888	0.23640	15.21
Mean value	1.3888	0.23640	15.21

Table A.4: Measured n and calculated values of F_n and δ for n -hexane.

n-hexane	n	F_n	δ_i [MPa ^{0.5}]
1	1.3828	0.23316	14.84
2	1.3828	0.23316	14.84
3	1.3827	0.23310	14.84
Mean value	1.3828	0.23314	14.84

Table A.5: Measured n and calculated values of F_n and δ for n -pentane.

n-pentane	n	F_n	δ_i [MPa ^{0.5}]
1	1.3644	0.22312	14.32
2	1.3644	0.22312	14.32
3	1.3644	0.22312	14.32
Mean value	1.3644	0.22312	14.32

A.1.2 $T = 323 \text{ K}$

Table A.6: The refractive index n and F_n for various hydrocarbons at $T = 323 \text{ K}$. α_p is the thermal expansion coefficient required for calculating δ_i (Li 2011).

Hydrocarbon	n	F_n	δ_i [MPa ^{0.5}]	$\alpha_p \times 10^3$ [1/K]
Hexane	1.3581	0.21965	14.14	1.41
Heptane	1.3723	0.22744	14.55	1.24
Octane	1.3880	0.23321	14.84	1.15
Decane	1.3983	0.24151	15.27	1.07
Dodecane	1.4088	0.24712	15.56	0.99
Cyclohexane	1.4156	0.24782	15.59	1.08
Toluene	1.4797	0.28383	17.46	1.27

A.2 Filtration with Hydrocarbons

Table A.7: Mixture compositions for the crude oil+toluene+*n*-heptane mixture, average amount of precipitated asphaltene including the standard deviation
and mixture solubility parameters.

Vol%(tol.)	<i>V</i> (tol.) [mL]	<i>V</i> (hep.) [mL]	<i>m</i> (paper) [g]	<i>m</i> (asph.+paper) [g]	Δ [g]	wt% asph.	δ _{mixture} [MPa ^{0.5}]
0	0	40	0.3054	0.4044	0.0990	10.07 ± 0.27	15.32
10	4	36	0.2964	0.3703	0.0739	7.52 ± 0.04	15.61
20	8	32	0.2956	0.3460	0.0504	5.13 ± 0.28	15.89
30	12	28	0.2944	0.3177	0.0233	2.37 ± 0.46	16.18
40	16	24	0.3030	0.3081	0.0051	0.52 ± 0.23	16.47
50	20	20	0.2974	0.2999	0.0025	0.25 ± 0.06	16.75
60	24	16	0.2976	0.3004	0.0028	0.28 ± 0.09	17.04
70	28	12	0.3001	0.3019	0.0018	0.18 ± 0.04	17.32
80	32	8	0.3034	0.3054	0.0020	0.20 ± 0.02	17.61
90	36	4	0.2942	0.2963	0.0021	0.21 ± 0.07	17.89
100	40	0	0.2988	0.3004	0.0016	0.16 ± 0.04	18.18

Table A.8: Mixture compositions for the crude oil+toluene+*n*-hexane mixture, amount of precipitated asphaltenes and mixture solubility parameters.

Vol%(tol.)	$V(\text{tol.})$ [mL]	$V(\text{hex.})$ [mL]	$m(\text{paper})$ [g]	$m(\text{asph.}+\text{paper})$ [g]	Δ [g]	wt% asph.	δ_{mixture} [MPa ^{0.5}]
0	0	40	0.3012	0.4112	0.1100	11.19	14.97
10	4	36	0.2945	0.3788	0.0843	8.58	15.29
20	8	32	0.3012	0.3591	0.0579	5.89	15.61
30	12	28	0.3002	0.3310	0.0308	3.13	15.93
40	16	24	0.2891	0.3057	0.0166	1.69	16.25
50	20	20	0.2955	0.2998	0.0043	0.44	16.57
60	24	16	0.3001	0.3013	0.0012	0.12	16.89
70	28	12	0.2999	0.3011	0.0012	0.12	17.22
80	32	8	0.2765	0.2800	0.0035	0.36	17.54
90	36	4	0.2981	0.3000	0.0019	0.19	17.86
100	40	0	0.3002	0.3022	0.0020	0.20	18.18

Table A.9: Mixture compositions for the crude oil+toluene+*n*-pentane mixture, amount of precipitated asphaltene and mixture solubility parameters.

Vol%(tol.)	V(tol.) [mL]	V(pen.) [mL]	m(paper) [g]	m(asph.+paper) [g]	Δ [g]	wt% asph.	δ _{mixture} [MPa ^{0.5}]
0	0	40	0.2888	0.4202	0.1314	13.37	14.46
10	4	36	0.2988	0.4000	0.1012	10.30	14.83
20	8	32	0.2958	0.3750	0.0792	8.06	15.21
30	12	28	0.2864	0.3351	0.0487	4.95	15.58
40	16	24	0.2992	0.3251	0.0259	2.63	15.95
50	20	20	0.3108	0.3210	0.0102	1.04	16.32
60	24	16	0.3001	0.3023	0.0022	0.22	16.69
70	28	12	0.3130	0.3150	0.0020	0.20	17.06
80	32	8	0.2989	0.3012	0.0023	0.23	17.44
90	36	4	0.2951	0.2988	0.0037	0.38	17.81
100	40	0	0.3004	0.3021	0.0017	0.17	18.18

A.3 Filtration at $T = 323\text{ K}$

Table A.10: Mixture compositions and amount of precipitated asphaltenes from a crude oil+heptol mixture at $T = 323\text{ K}$.

Vol%(tol.)	$V(\text{tol.})$ [mL]	$V(\text{hep.})$ [mL]	$m(\text{paper})$ [g]	$m(\text{asph.}+\text{paper})$ [g]	Δ [g]	wt% asph.
0	0	40	0.2995	0.3933	0.0938	9.54
10	4	36	0.3004	0.3707	0.0703	7.15
20	8	32	0.2985	0.3454	0.0469	4.77
30	12	28	0.2967	0.3167	0.0200	2.03
35	14	26	0.2986	0.3074	0.0088	0.90
40	16	24	0.3017	0.3034	0.0017	0.17
45	18	22	0.3001	0.3014	0.0013	0.13
50	20	20	0.2934	0.2947	0.0013	0.23
60	24	16	0.2999	0.3014	0.0015	0.15
70	28	12	0.3002	0.3004	0.0002	0.02

A.4 Enthalpy of Vaporisation

The following data were taken from Linstrom and Mallard (2010).

Table A.11: Enthalpy of vaporisation at different temperatures.

(a) Enthalpy of vaporisation of toluene.
With, $T_c = 591.7$ K; $A = 53.09$ kJ/mol;
 $\beta = 0.2774$

T [K]	T_r [K]	ΔH [kJ/mol]
298	0.50	38.01
300	0.51	37.91
305	0.52	37.64
310	0.52	37.37
315	0.53	37.09
320	0.54	36.82
323	0.55	36.66
330	0.56	36.27
335	0.57	35.99
340	0.57	35.71
345	0.58	35.43
350	0.59	35.13
355	0.60	34.86
360	0.61	34.58

(b) Enthalpy of vaporisation of heptane.
With, $T_c = 540.2$ K; $A = 53.66$ kJ/mol;
 $\beta = 0.2831$

T [K]	T_r [K]	ΔH [kJ/mol]
298	0.55	36.58
300	0.56	36.45
305	0.56	36.14
310	0.57	35.83
315	0.58	35.51
320	0.59	35.20
323	0.60	35.00
330	0.61	34.55
335	0.62	34.23
340	0.63	33.90
345	0.64	33.57
350	0.65	33.24
355	0.66	32.90
360	0.67	32.56

A.5 HPHT Filtration

Table A.12: Precipitated asphaltenes from the diluted crude oil with CO₂ for the pressure range investigated at $T = 323$ K. A constant amount of residual (res.) oil on the filter paper after filtration was subtracted from Δ .

p [bar]	$m(\text{dil. oil})$ [g]	$m(\text{paper})$ [g]	$m(\text{residue}+\text{paper})$ [g]	Δ [g]	$m\text{-res.oil}^a$ [g]	wt% asph.
30	11.8012	0.3022	0.3977	0.0955	0.0094	0.1119
40	11.9524	0.2999	0.3908	0.0909	0.0048	0.0571
50	12.1768	0.3047	0.3908	0.0861	0.0000	0.0000
60	12.0043	0.3027	0.3979	0.0952	0.0091	0.1083
70	12.2435	0.3102	0.4048	0.0946	0.0085	0.1012
80	12.0637	0.3007	0.3921	0.0914	0.0053	0.0631
100	12.1000	0.3081	0.4278	0.1197	0.0336	0.4000
120	12.0301	0.3138	0.4545	0.1407	0.0546	0.6500
140	12.2252	0.2946	0.5067	0.2121	0.1260	1.5000
160	12.0825	0.2865	0.5490	0.2625	0.1746	2.1000
180	12.1720	0.3149	0.5877	0.2728	0.1867	2.2226
200	11.9407	0.2893	0.6363	0.3470	0.2609	3.1060
220	12.3961	0.3121	0.7114	0.3993	0.3132	3.7286
240	11.4342	0.3014	0.7584	0.4570	0.3709	4.4155

^a0.0861 g

Table A.13: HPHT filtration experiments with Helium and diluted crude oil for the pressure range investigated at $T = 323$ K.

p [bar]	$m(\text{dil. oil})$ [g]	$m(\text{paper})$ [g]	$m(\text{residue}+\text{paper})$ [g]	Δ [g]	$m\text{-res.oil}^a$ [g]	wt% residue
20	12.1654	0.2991	0.4108	0.1117	0.0256	0.0030
40	12.8507	0.3002	0.4307	0.1305	0.0444	0.0049
80	12.2315	0.3000	0.3983	0.0983	0.0122	0.0014
120	12.4193	0.3053	0.4004	0.0951	0.0090	0.0010
160	11.9179	0.3011	0.4077	0.1066	0.0205	0.0025

^a0.0800 g

Table A.14: HPHT filtration experiments with the original crude oil for the pressure range investigated at $T = 323$ K.

p [bar]	$m(\text{oil})$ [g]	$m(\text{paper})$ [g]	$m(\text{residue}+\text{paper})$ [g]	Δ [g]	$m\text{-res.oil}^a$ [g]	wt% asph.
20	1.6760	0.2996	0.4355	0.1359	0.0059	0.3520
60	3.7337	0.2967	0.4579	0.1612	0.0312	0.8356
100	2.4442	0.2986	0.4383	0.1397	0.0097	0.3969
140	1.7318	0.2972	0.5311	0.2339	0.1039	5.9995
180	1.7930	0.3002	0.5950	0.2948	0.1648	9.1913
220	1.7630	0.3038	0.6831	0.3793	0.2493	14.1407

^a0.1300 g

A.6 The Solubility Parameter of CO₂

- Critical pressure CO₂

$$p_c = 7.38 \text{ MPa (taken from NIST (Linstrom and Mallard 2010))}$$

- Critical temperature CO₂

$$T_c = 304.1 \text{ K (taken from NIST (Linstrom and Mallard 2010))}$$

- Internal energy isothermally expanded to “zero” pressure CO₂

$$E^* = 20.555 \text{ kJ/mol (extrapolated from Table A.15).}$$

Table A.15: Thermophysical data and calculation of δ_{CO_2} for CO₂ at various pressures and $T = 323 \text{ K}$.

p [bar]	p [MPa]	$\rho(\text{CO}_2)$ [kg/m ³]	E [kJ/mol]	Z	$m(\text{CO}_2)$ [g]	δ_{CO_2} [MPa ^{0.5}]
10	1	17.05	20.31	0.96	8.32	0.31
20	2	35.62	20.04	0.92	17.38	0.65
30	3	56.07	19.75	0.88	27.36	1.01
40	4	78.92	19.43	0.83	38.52	1.42
50	5	104.95	19.07	0.78	51.22	1.88
60	6	135.39	18.66	0.73	66.07	2.41
70	7	172.31	18.18	0.67	84.08	3.05
80	8	219.73	17.59	0.60	107.23	3.85
90	9	286.12	16.80	0.51	139.63	4.94
100	10	386.77	15.73	0.42	188.74	6.51
120	12	587.07	13.88	0.39	286.49	8.70
140	14	673.70	13.11	0.37	328.77	10.31
160	16	723.27	12.65	0.36	352.96	11.37
180	18	758.11	12.33	0.39	369.96	11.88
200	20	785.16	12.07	0.42	383.16	12.30
220	22	807.39	11.86	0.45	394.01	12.63
240	24	826.35	11.67	0.48	403.26	12.91
260	26	842.92	11.51	0.51	411.34	13.16
280	28	857.69	11.36	0.53	418.55	13.39
300	30	871.03	11.23	0.56	425.06	13.59

Table A.16: Partial molar volume, mole fraction and mixture solubility parameter of the original crude oil and CO₂ in the pressure cell for the pressure range investigated at $T = 323$ K.

p [bar]	$w(\text{CO}_2)^a$	$x(\text{CO}_2)$	$x(\text{oil})$	$\rho(\text{oil})$ [g/mL]	$V_{\text{m,oil}}$ [mL/mol]	$V_{\text{m,CO}_2}$ [mL/mol]	δ_{mixture} [MPa ^{0.5}]
20	0.0054	0.0612	0.9388	0.984	537.6	1235.4	17.03
60	0.0395	0.3310	0.6690	0.986	536.5	325.1	15.93
100	0.1133	0.6057	0.3943	0.988	535.5	113.8	15.69
140	0.1384	0.6587	0.3413	0.990	534.4	65.3	16.82
180	0.1519	0.6829	0.3171	0.992	533.3	58.1	16.97
220	0.1622	0.6994	0.3006	0.994	532.3	54.5	16.95

^a(Hu et al. 2016; Hu 2016)

Appendix B

Aspen Input Summary

```
;
;Input Summary created by Aspen Properties Rel. 30.0

PROP

IN-UNITS MET

DESCRIPTION "
  Polymers Simulation with Metric Units :
  K, atm, kg/hr, kmol/hr, cal/sec, l/min.

  Property Method: None

  Flow basis for input: Mass

  Stream report composition: Mass flow
"

DATABANKS 'APV84 POLYMER' / 'APV84 SEGMENT' / 'APV84 INITIATO' &
          / 'APV84 PC-SAFT' / 'APV84 PURE28' / NOASPENPCD

PROP-SOURCES 'APV84 POLYMER' / 'APV84 SEGMENT' / &
             'APV84 INITIATO' / 'APV84 PC-SAFT' / 'APV84 PURE28'

COMPONENTS
  STY-SEG C8H8-R /
  POLY /
  EICOSANE C20H42 /
  CUMENE C9H12-2 /
  DODECANE C12H26 /
  HEPTANE C7H16-1

ADA-SETUP
  ADA-SETUP PROCEDURE=REL9
```

GROUPS CH3 1015 / CH2 1010 / ACCH 1150 / ACH 1105 /

PROPERTIES POLYUFV

PROPERTIES POLYFH / POLYNRTL / POLYSL / POLYUF

STRUCTURES

UNIFAC CUMENE 1015 2 / 1105 5 / 1150 1

UNIFAC DODECANE 1015 2 / 1010 10

UNIFAC EICOSANE 1015 2 / 1010 18

UNIFAC HEPTANE 1010 5 / 1015 2

UNIFAC POLY 1015 2 / 1010 9 / 1150 9 / 1105 45

PROP-DATA US-3

IN-UNITS MET

PROP-LIST PC / ZC / TC

PVAL POLY 20 / 0.2 / 1000

PROP-DATA PLXANT-1

IN-UNITS MET PRESSURE=psig PDROP=atm

PROP-LIST PLXANT

PVAL POLY -10 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1000.000

PROP-DATA U-1

IN-UNITS MET

PROP-LIST GMUFR / GMUFQ

PVAL CH3 0.9011 / 0.848

PVAL CH2 0.6744 / 0.64

PVAL ACH 0.5313 / 0.4

PVAL ACCH 0.8121 / 0.348

PROP-DATA GMUFB-1

IN-UNITS MET

PROP-LIST GMUFB

BPVAL ACCH ACCH 0

BPVAL ACCH ACH -146.8

BPVAL ACCH CH2 -69.70

BPVAL ACCH CH3 -69.70

BPVAL ACH ACCH 167

BPVAL ACH ACH 0

BPVAL ACH CH2 -11.12

BPVAL ACH CH3 -11.12

BPVAL CH2 ACCH 76.50

BPVAL CH2 ACH 61.13

BPVAL CH2 CH2 0

BPVAL CH2 CH3 0

BPVAL CH3 ACCH 76.50

BPVAL CH3 ACH 61.13

BPVAL CH3 CH2 0

BPVAL CH3 CH3 0

POLYMERS

SEGMENTS STY-SEG REPEAT

OLIGOMERS POLY STY-SEG 9.

PROP-SET PS-1 MOLEFRAC SUBSTREAM=MIXED PHASE=V L L1 L2 T

PROPERTY-REP PCES NOPARAM-PLUS

```
PROP-TABLE PT-1 FLASHCURVE
  BLOCK-OPTION FREE-WATER=NO
  MOLE-FLOW POLY 0.001 / EICOSANE 0.335 / CUMENE 0.321 / &
    DODECANE 0.343 / HEPTANE 0.5
  STATE PRES=1. <MPa>
  VARY TEMP
  RANGE LOWER=290. UPPER=600. INCR=1.
  PARAM NPHASE=3
  TABULATE PROPERTIES=PS-1
;
```


Appendix C

SRD Input File

C.1 Example for an SRD Input File for $Pe = 10$ and $\varepsilon_{a-a} = 5 \text{ kT}$

```
### colloid parameters #####
700      ;number of colloids
0.0      ;fraction of colloids pulled in opposite direction
50.      ;mass of colloid          (solvent masses)
3.0      ;colloid diameter         (lattice spacings)
0.0d0    ;LJ repulsive strength    (kT)
48       ;LJ steepness, ie 48 -> 48-24 potential
2.5d0    ;colloid-solvent LJ repulsive strength (always 12-6)
-124.4d0 ;Yukawa 1 interaction strength (kT)
124.4d0  ;Yukawa 2 interaction strength (kT)
9d0      ;Yukawa 1 inverse screening length (inv.latt.spacings)
10.d0    ;Yukawa 2 inverse screening length (inv.latt.spacings)
5.d0     ;Yukawa cut-off radius     (lattice spacings)
500.0    ;colloidal friction (Brownian case)
### depletant (polymer) parameters #####
0        ;number of depletants
100.0    ;mass of depletant         (solvent masses)
0.8      ;radius of gyration of depletant (lattice spacings)
0.d0     ;pol-pol interaction strength (kT)
10.0     ;depletant friction (Brownian case)
### solvent parameters #####
155260   ;number of solvent particles
1.3      ;colloid-solvent interaction radius
10       ;number of MD steps between each collision (icol)
### simulation parameters #####
```

```

0.01      ;MD time step
10000000  ;total number of steps
1720000   ;max. CPU time
20000     ;save interval
0         ;continuation run (1) or not (0)
16        ;list radius for depletant cell linked list
80        ;number of cells in x-direction
450       ;number of cells in y-direction
1         ;walls (1) or periodic boundaries (0) in x-direction
0         ;walls (1) or periodic boundaries (0) in y-direction
0         ;scrambling interval for y boundary (0 turns scrambling off)
0         ;use (1) or don't use (0) flowing boundary conditions
0.0       ;solvent inflow velocity (in case of flowing boundary)
1         ;use thermostat on system (1) or not (0)
1         ;hydrodynamics (1), velocity exchange (0), or Brownian (-1)
1.341d-4  ;external force on solvent (pos.) or colloids (neg.)
0.0d-4    ;gravitation on colloids in x-direction
0.0       ;switching frequency for external force
0         ;fix solvent centre-of-mass (1) or total centre of mass (-1)
0         ;fix depletant centre-of-mass
0         ;fix EACH colloid
### analysis parameters #####
0         ;force autocorrelation sample interval
1000      ;velocity autocorrelation sample interval
1000      ;coarse-grained velocity interval
0         ;stress tensor sample interval
0         ;dynamic structure factor sample interval
0         ;density map sample interval (pos: z-rho plane; neg: z-x plane)
1.0       ;density map bin width (dbin)
0         ;colloidal radial distribution sample interval
0.2       ;g(r) bin width
0         ;order parameter sample interval
-20000    ;PDB output interval (negative=movie)
2.8       ;colloid-colloid alarm proximity
1.1       ;colloid-solvent alarm proximity
0         ;ranged order parameter sample interval
0         ;no of ranges at which to measure the order parameter
0         ;difference between ranges for order parameter measurement
0         ;order parameter measurement bin height (0 = whole box)
0         ;range to use for colouring laned/unlaned colloids in pdb file
1000      ;radius of gyration measurement interval
6.5       ;separation at which two colloids are considered to be touching
5         ;minimum cluster size for consideration in
          calculating fractal dimension

```

Appendix D

Core Holder Design

D.1 Main Body

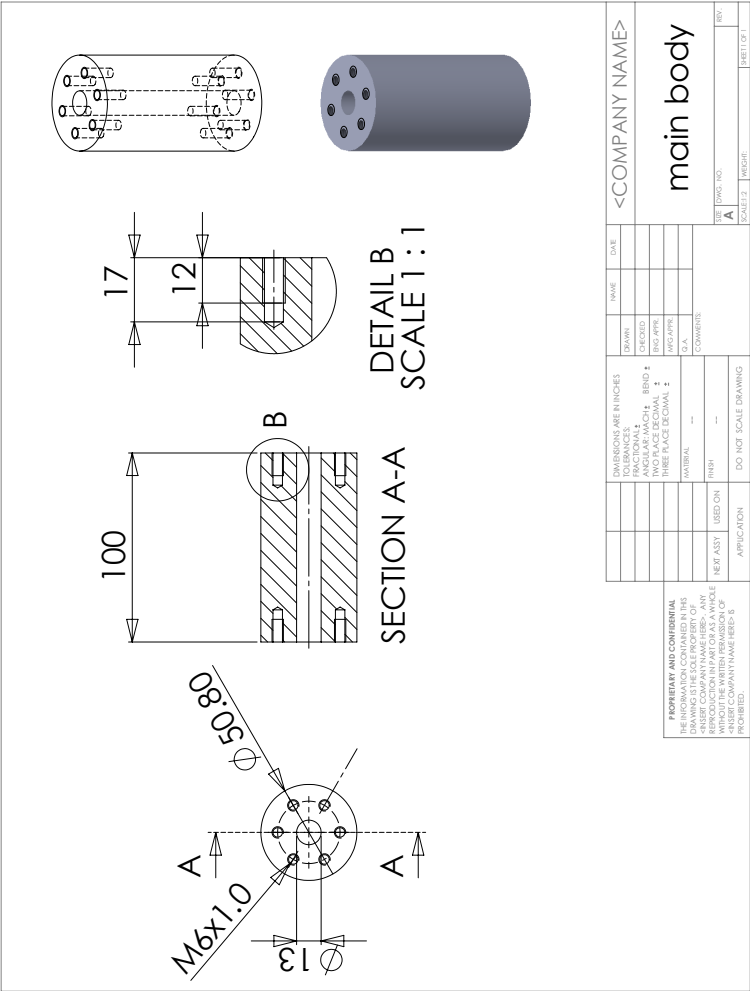


Figure D.1: Technical drawing of the coreholder main body. All dimensions are given in mm.

D.2 End Cap - Inlet

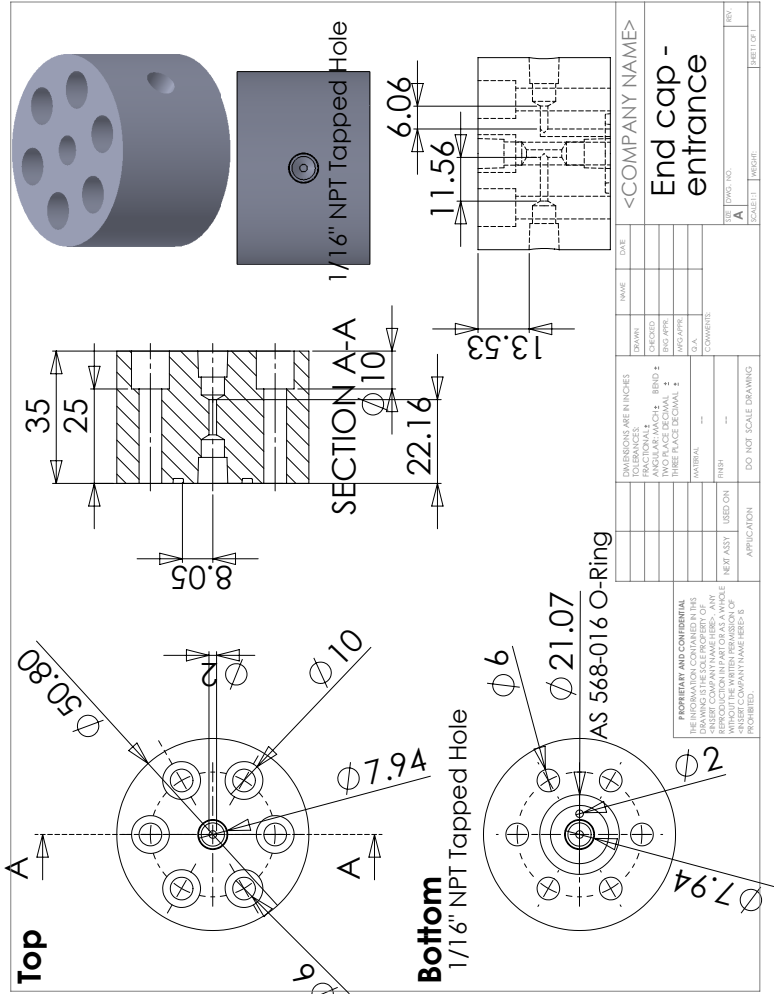


Figure D.2: Technical drawing of the coreholder inlet end cap. All dimensions are given in mm.

D.3 End Cap - Outlet

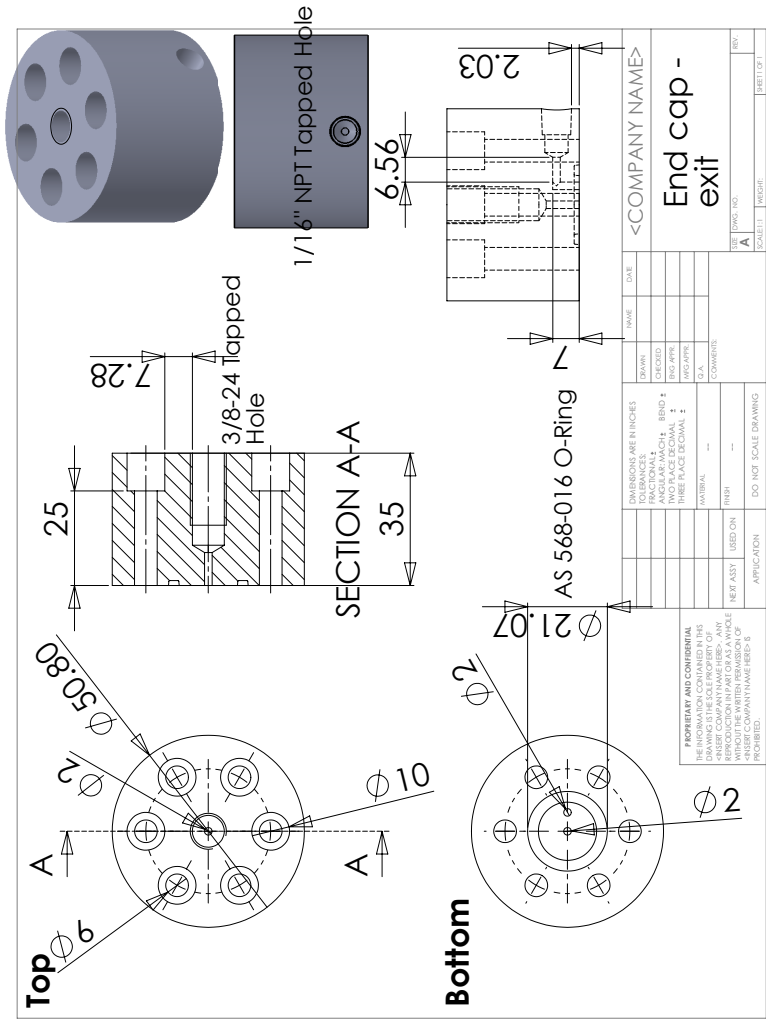


Figure D.3: Technical drawing of the coreholder outlet end cap. All dimensions are given in mm.

Appendix E

Pressure Transducer Calibration

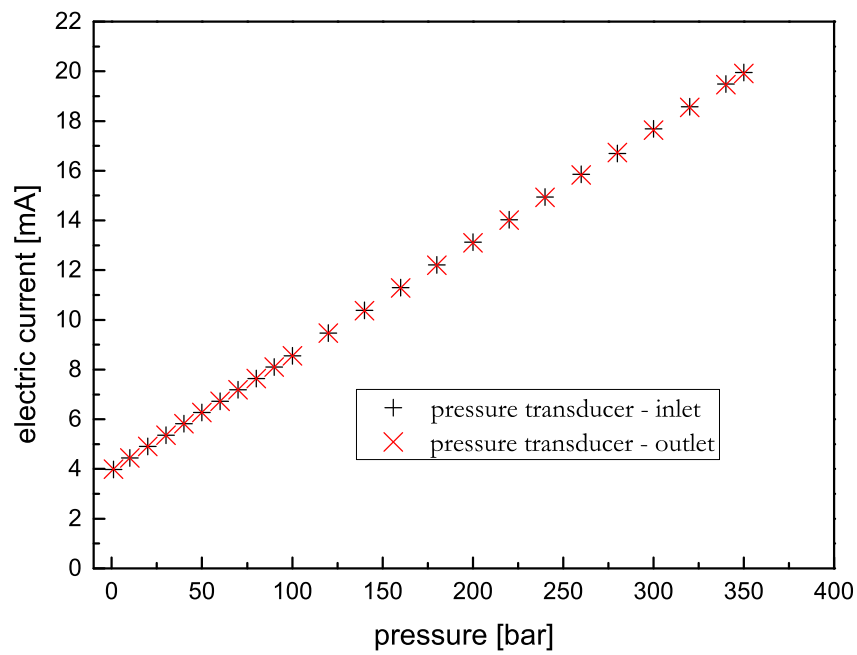


Figure E.1: Pressure transducer calibration.

Appendix F

Supplementary MicroCT Images

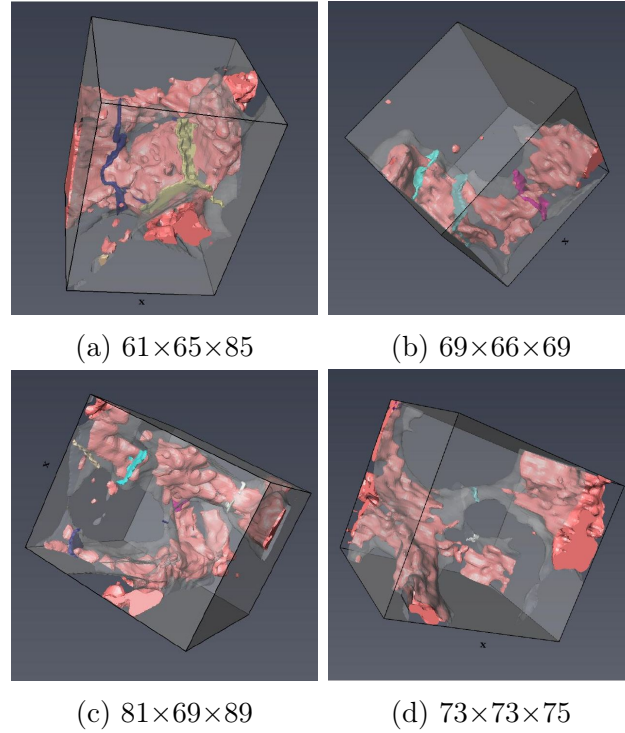


Figure F.1: Supplementary microCT images (voxel size = $2.1 \mu\text{m}$) showing predominately pore throat deposition and plugging of CO_2 -asphaltenes. The grey grains were rendered semi-transparent, the asphaltenes are shown in salmon and the pore throats are marked in different colours. The lattice in the x -dimension is labelled accordingly.

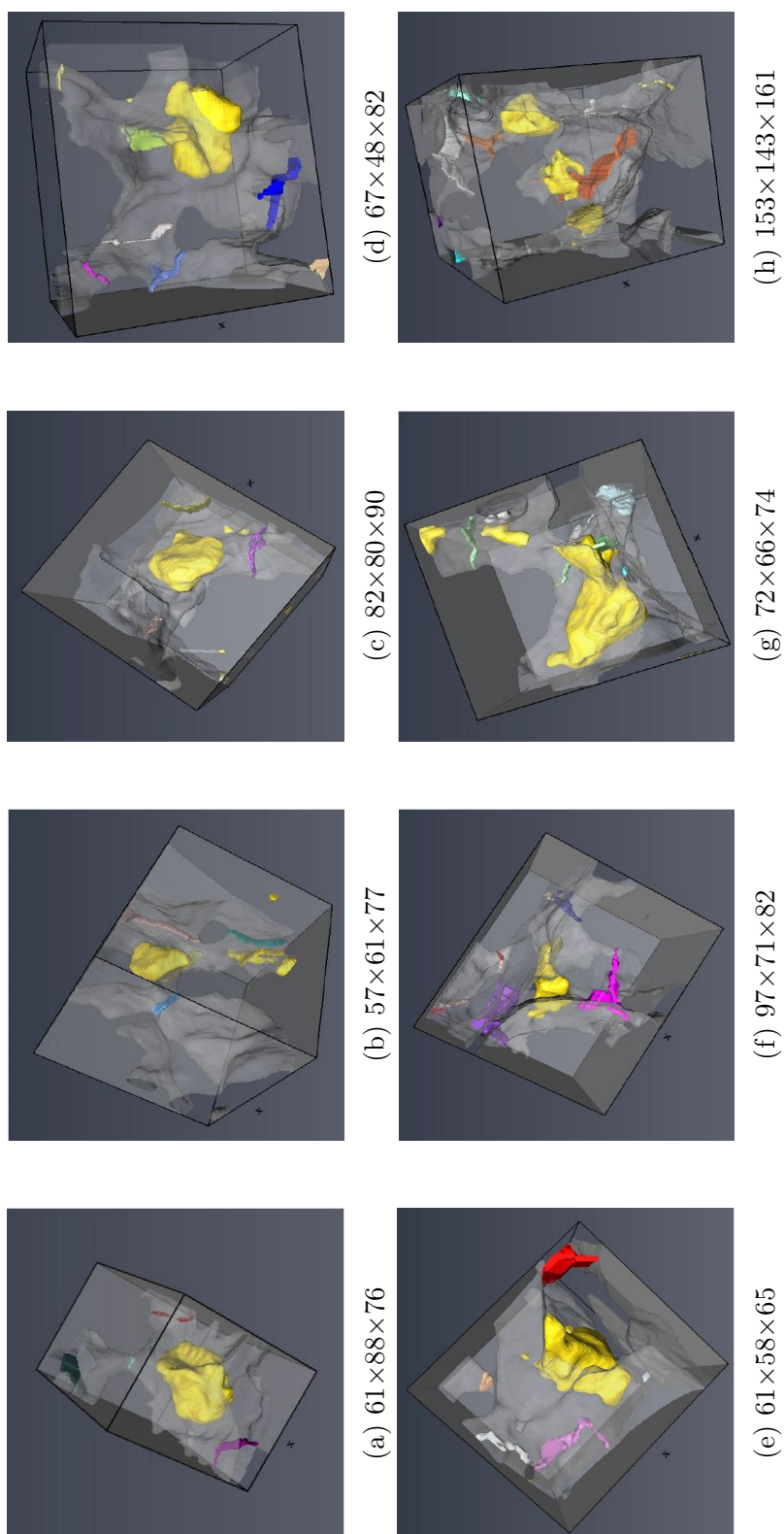


Figure F.2: Supplementary microCT images (voxel size = $2.1 \mu\text{m}$) showing predominately pore surface deposition of C7-asphaltenes. The grey grains were rendered semi-transparent, the asphaltenes are shown in yellow and the pore throats are marked in different colours. The lattice in the x -dimension is labelled accordingly.

Appendix G

DBF Main Input File

G.1 Example for an DBF Input File ($Q_t = 50$ $\mu\text{L}/\text{min}$)

```
-----
- E300 Asphaltene Option
- Bentheimer, Flow rate = 0.05 mL/min
- Adapted from GF3_base_asp (Boek et al. (2011), SPE 147539)
  by Christine M. Seifried (cms)
- EoS mode in E300
- Grid dimensions 10*1*1
- FIELD units
-----

RUNSPEC =====
TITLE
  Asphaltene deposition
START
  1 Jan 2015  /
LAB
GAS
OIL
DIMENS
- cms: blocks in X,Y,Z direction
  10 1 1  /
COMPS
```

```
- cms: C7, Tol, ASP, flocs
4 /
```

```
-AIM
FULLIMP
```

```
NOECHO
```

```
INCLUDE
'ASP_RUNSPEC.INC' /
```

```
GRID =====
```

```
-Basic grid block sizes
```

```
EQUALS
```

```
DX 0.1745 / 0.019685 /
DY 1.676 / 0.066874 /
DZ 1.676 / 0.066874 /
PORO 0.194 /
PERMX 969.5 /
PERMY 969.5 /
PERMZ 969.5 /
TOPS 0 /
/
```

```
- Depths of the top face of each grid block (ft)
```

```
PROPS =====
```

```
-Gas saturation functions
```

```
SGFN
```

```
- cms: SG gasrelperm gas-oil_cap.pressure
0.00 0.000 0.0
0.04 0.005 0.0
0.12 0.026 0.0
0.24 0.078 0.0
0.36 0.156 0.0
0.48 0.260 0.0
0.60 0.400 0.0
0.72 0.562 0.0
-0.84 0.8 0.0
1.00 0.8 0
/
```

```
-cms: last row added
```

```
-Oil saturation functions
```

```
SOF2
```

```
- cms: OS oilrelperm
0.00 0.000
0.24 0.000
0.28 0.005
```

```

0.32  0.012
0.44  0.100
0.56  0.400
0.72  0.800
0.84  1.000
1.00  1.000  /

```

-Rock properties

ROCK

```

- pres (atm)    cw (1/atm)
      1  5.0E-5  /

```

- Water properties
- Standard conditions

STCOND

-Temp Pressure

```

-
      25          1  /

```

-cms: p = 1

- PVT model from PVTi - do not comment it out.

INCLUDE

'bent_50_asp.PVO' /

INCLUDE

'ASP_PROPS.INC' /

SOLUTION =====

PRESSURE

10*1 /

-cms: changed from 10 to 1

-cms: SGAS added, error: GAS saturation not specified

SGAS

10*0.00

-10*0.04

-0.12

-0.24

-0.36

-0.48

-0.60

-0.72

-0.84

-1.00

/

ZMF

-cms: composition

10*0

10*0

10*0

10*0

```

10*0
10*0
10*0
10*0
10*0
10*0.295981426
10*0.700604322
10*0.001707126
10*0.001707126
/

```

```

RPTRST
PRESSURE SOIL SGAS  XMF YMF
RPORV /
- cms: no SWAT

```

```

SUMMARY  =====

```

```

- cms:
EXCEL

```

```

FGPR
FOPR
FOIR
- cms: changed FLIR to FGIR
FGIR
FOPT
FPR
FOSAT
FGSAT

```

```

WBHP
  PROD  WINJ  /

```

```

TCPU
ELAPSED
NEWTON

```

```

BMLSC
- block component
  1  1  1 11 /
  2  1  1 11 /
  3  1  1 11 /
  4  1  1 11 /
  5  1  1 11 /
  6  1  1 11 /
  7  1  1 11 /
  8  1  1 11 /
  9  1  1 11 /
 10  1  1 11 /
/

```

```

BMLSC
- block component
  1  1  1 12 /
  2  1  1 12 /

```

```

3 1 1 12 /
4 1 1 12 /
5 1 1 12 /
6 1 1 12 /
7 1 1 12 /
8 1 1 12 /
9 1 1 12 /
10 1 1 12 /
/

```

- Other block parameters

BXMF

```

1 1 1 12 /
2 1 1 12 /
3 1 1 12 /
4 1 1 12 /
5 1 1 12 /
6 1 1 12 /
7 1 1 12 /
8 1 1 12 /
9 1 1 12 /
10 1 1 12 /
1 1 1 13 /
2 1 1 13 /
3 1 1 13 /
4 1 1 13 /
5 1 1 13 /
6 1 1 13 /
7 1 1 13 /
8 1 1 13 /
9 1 1 13 /
10 1 1 13 /
/

```

BPR

```

1 1 1 /
2 1 1 /
3 1 1 /
4 1 1 /
5 1 1 /
6 1 1 /
7 1 1 /
8 1 1 /
9 1 1 /
10 1 1 /
/

```

BDENO

```

1 1 1 /
2 1 1 /
3 1 1 /
4 1 1 /
5 1 1 /
6 1 1 /
7 1 1 /
8 1 1 /

```

```

  9  1  1  /
10  1  1  /
/

```

BPORV

```

  1  1  1  /
  2  1  1  /
  3  1  1  /
  4  1  1  /
  5  1  1  /
  6  1  1  /
  7  1  1  /
  8  1  1  /
  9  1  1  /
10  1  1  /
/

```

BOVIS

```

  1  1  1  /
  2  1  1  /
  3  1  1  /
  4  1  1  /
  5  1  1  /
  6  1  1  /
  7  1  1  /
  8  1  1  /
  9  1  1  /
10  1  1  /
/

```

INCLUDE

```
'ASP_SUMMARY.INC' /
```

RUNSUM

```
SCHEDULE =====
```

```
- Reporting frequency
```

RPTRST

```
PRESSURE SOIL SGAS XMF YMF
RPORV ASPFLO /
```

```
- cms: no SWAT
```

```
-Define injection and production wells
```

WELSPECS

```

- Well  Group  IO JO  depth  phase
  WINJ   FIELD   1  1    1*    OIL  /
  PROD   FIELD  10  1    1*    OIL  /
/

```

COMPDAT

```
-cms: diameter changed from 0.5 to 0.1
```

```
- Well  I  J  K1  K2  Status  *  * diameter - wellbore radius = 0.5 cm
```

```

    WINJ  1  1  1  1  OPEN  2*  0.01 /
    PROD 10  1  1  1  OPEN  2*  0.01 /
/

WCONPROD
- Well Status Mode Orat Wrat Grat Lrat Resv BHP
  PROD  OPEN  BHP  1*  1*  1*  1*  1*  1 /
/
-cms: BHP changed from 10 to 1

WELLSTRE
-cms: composition changed
- name
  IOIL
  0
  0
  0
  0
  0
  0
  0
  0
  0
  0
0.295981426
0.700604322
0.001707126
0.001707126
/
/

WINJOIL
-cms: changed from WINJGAS to WINJOIL
- Well Type Stream
  WINJ  STRE  IOIL  /
/

WCONINJE
- Well Type Status Mode Surf Resv BHP
- cms: 10cm3/h (flow rate used in Minsseuix, 1997 for GF3)
- cms: RATE = surface flow rate target
- cms: 50 microL/min = 0.05 mL/min = 3 cm3/hr
  WINJ  HCOIL OPEN  RATE  3  1* 10.0  /
/
-cms: HCOIL was originally GAS

WELOPEN
- name status
  PROD  OPEN  /
  WINJ  OPEN  /
/

NEXTSTEP
  0.01  /

TSTEP

```

60*5 /

END