

Catalytic depolymerization of lignin with
simultaneous direct methane aromatization in a
fluidized bed reactor

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Abstract

Rapid population growth and increasing industrialisation in developing countries pushes the need for more energy and high added-value chemicals sources to be developed and utilized. Biomass and lignin pyrolysis in H_2 atmosphere is a promising method to generate aromatics, in particular mixtures of benzene, toluene, xylene and ethylbenzene (BTEX), which represent a higher added-value product than fuels. The source of H_2 for lignin depolymerization is important, as high purity H_2 is a relatively expensive gas and it there might be some safety concerns associated to transport and storage. Direct CH_4 aromatization (DMA) is a promising reaction to generate in-situ H_2 and C_6H_6 . The optimal operating conditions as well as nature of catalysts able to promote both lignin depolymerization and DMA to generate higher H_2 and oil yields have become an interesting topic to study.

This work used a laboratory scale continuous pressurized fluidized bed reactor to study the DMA reaction between 550 °C and 700 °C at 1 bar. The DMA reaction was used to provide H_2 in-situ, which can help to upgrade lignin pyrolysis. The same fluidized bed reactor was also used to investigate CH_4 and lignin simultaneous pyrolysis with different catalysts and a range of operating conditions. A fixed bed was designed and placed downstream from the fluidized bed to enable experiments with a two-stage system, employing both in-situ and ex-situ catalysts in the simultaneous pyrolysis of CH_4 and lignin at 580 °C.

The main findings can be summarized as: (1) a $Ni/Al_2O_3-SiO_2$ catalyst was observed to generate the highest H_2 and oil yield under 580 and 600 °C. The injection of a small amount of external H_2 before CH_4 injection can decrease the deactivation of Ni catalyst. (2) in this experimental system, the most important variables to increase oil yields in CH_4 and lignin simultaneous pyrolysis were total inlet gas flow rate and pressure. Lower total inlet gas flow rate can extend the residence time of small particle size lignin and volatiles in the catalytic bed, and pressure can significantly reduce the H_2 and oil generated by DMA reaction. (3) a $Ni/Al_2O_3-SiO_2$ catalyst led to the highest monoaromatics yields while a TiO_2 catalyst produced the highest total oil yield. The two-stage system with a $Ni/Al_2O_3-SiO_2$ catalyst represented a clear improvement on total oil yield and lignin conversion than a single bed.

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Declaration of Originality

I certify that all work presented in this thesis is my own and otherwise is appropriately referenced.

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List of abbreviations and Nomenclature

ACF	Active carbon fibers
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
BTEX	Benzene, toluene, ethylbenzene and xylenes
BTX	Benzene, toluene and xylenes
CF	Correction factor
CFB	Circulating fluidized bed
CI	Confidence intervals
CNF	carbon nanofibers
DI	Deionized
DMA	Non-oxidative direct methane aromatization
FBP	Fixed bed pyrolyzers
GC-FID	Gas Chromatography Flame Ionization Detector
GC-MS	Gas chromatography mass spectrometry
GC-TCD	Gas chromatography with a t-Thermal conductivity detector
GHG	Greenhouse gas
IR	Infrared
KL	Kraft lignin
RF	Response factor
S_{BET}	Specific surface area
SD	Standard deviation
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
TOS	Time on stream
XRD	X-ray diffraction

XRF

X-ray fluorescence

A_{gas1}	Peak area of single gas 1	-
CD	Drag coefficient	-
C_{gas1}	Concentration of single gas 1	-
C_{H2}	H ₂ concentration	Vol. %
C_p	Specific heat	J g ⁻¹ K ⁻¹
d	Interplanar distance	nm
D_i	Internal diameter	mm
d_p	Particle diameter	m
e	Minimal wall thickness	mm
f	Creep strength	MPa
g	Gravity acceleration	9.81 m s ⁻²
L_C	Lignin conversion rate	%
Re_p	Particles Reynold's number	
n	Positive integer	
N	Total moles of gas	mol
N_C	Moles of carbon deposited	mol
$N_{\text{C-oil}}$	Moles of C in the oil	mol
$N_{\text{(H2)}}$	Total mol of H ₂ produced at	mol
	Steady state	
$N_{\text{(CH4)}}$	Total moles of CH ₄ fed into	mol
	reactor during steady state	
S_C	Selectivity to carbon	%
S_{oil}	Selectivity to oil	%
$W_{\text{(CH4)}}$	Total weight of CH ₄	g
$W_{\text{chloroform}}$	Weight of chloroform left in	g
	the oil	
W_L	Lignin fed during the run	g

W_{L-oil}	Oil weight yield from lignin	g
W_{known}	Weight of compounds detected by GC-FID and confirmed by GC-MS	g
W_{oil}	Total oil weight	g
$W_{unknown}$	Weight of compounds out of GC range	g
W_{URL}	Weight of unreacted lignin	g
W_X	Weight of fraction X (oil, gas or solid product) recovered from the run	g
$Y_{(CH_4)}$	mol fraction of CH ₄	%
μ	Viscosity	kg m ⁻¹ s ⁻¹
ρ_g	Gas density	Kg m ⁻³
ρ_s	Solid density	Kg m ⁻³
ϕ_s	Sphericity	
ε_{mf}	Void fraction	
θ	Scattering angle	°
λ	Wavelength of incident ray	nm
Δt	Time interval	min
ΔV	Gas volume difference	L

Chapter 1. Introduction

1.1 Background

Rapid population growth and increasing industrialisation in developing countries pushes the need for more energy sources to be developed and utilized. According to BP's review,^[1] the world total consumption of energy constantly increased in the past 10 years (except in 2020, whose consumption was affected by the COVID-19 pandemics), as shown in Figure 1.1.

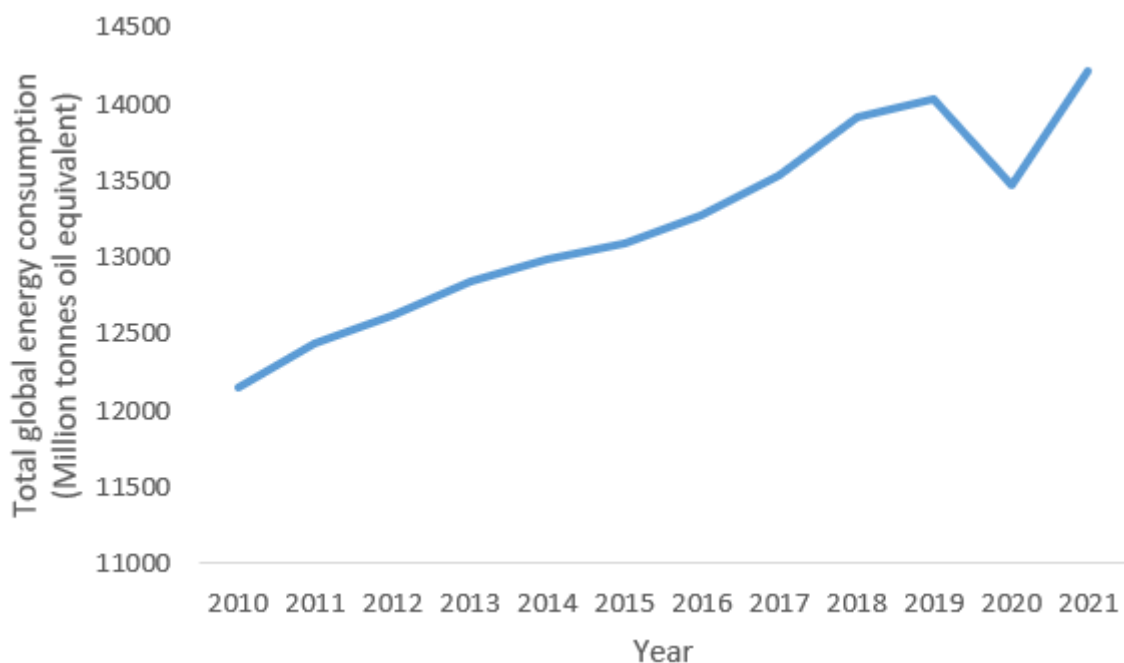


Figure 1.1 Total global energy consumption between 2010 and 2021 adapted from BP energy report^[1]

Renewable energy sources, considered as alternative to fossil energy, have been widely used in the world and their demand is constantly increasing in this century. According to BP's review, the percentage of renewable energy (except hydro energy) in global primary energy has exceeded that of nuclear energy in 2019 and reached the same level as hydroelectricity (Figure 1.2).

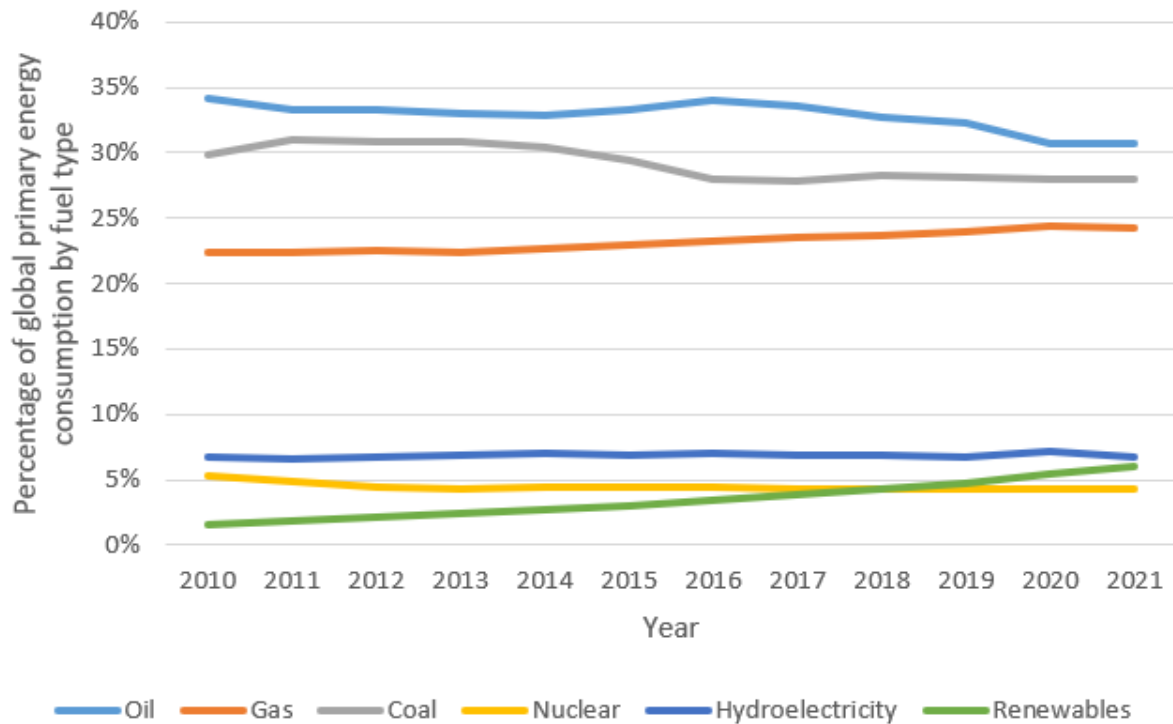


Figure 1.2 Percentage of global primary energy consumption by fuel type between 2010 and 2021 adapted from BP energy report ^[1]

Biomass is a greenhouse gas neutral renewable energy source which is abundant and widely distributed in the world. Compared with fossil energy, the utilization of biomass will not increase the amount of greenhouse gas emissions.

Solving the problem of climate change is considered as one of the major projects that should be faced in the 21st century. The reasons behind climate change can be divided into human and non-human contributions. Fossil fuel utilisation, especially after the industrial revolution, increased the emissions of primary greenhouse gas. The main primary greenhouse gas pollutants are CO₂ (emission amount shown in Figure 1.3), methane and nitrous oxide gas. The source of these gases is mainly fossil fuel burning and methane generated from cattle farming. Fossil fuels stored the carbon which existed in the atmosphere several billion years ago, which is released as CO₂ upon burning, changing the carbon balance of the atmosphere and becoming a crucial contributing factor to climate change.

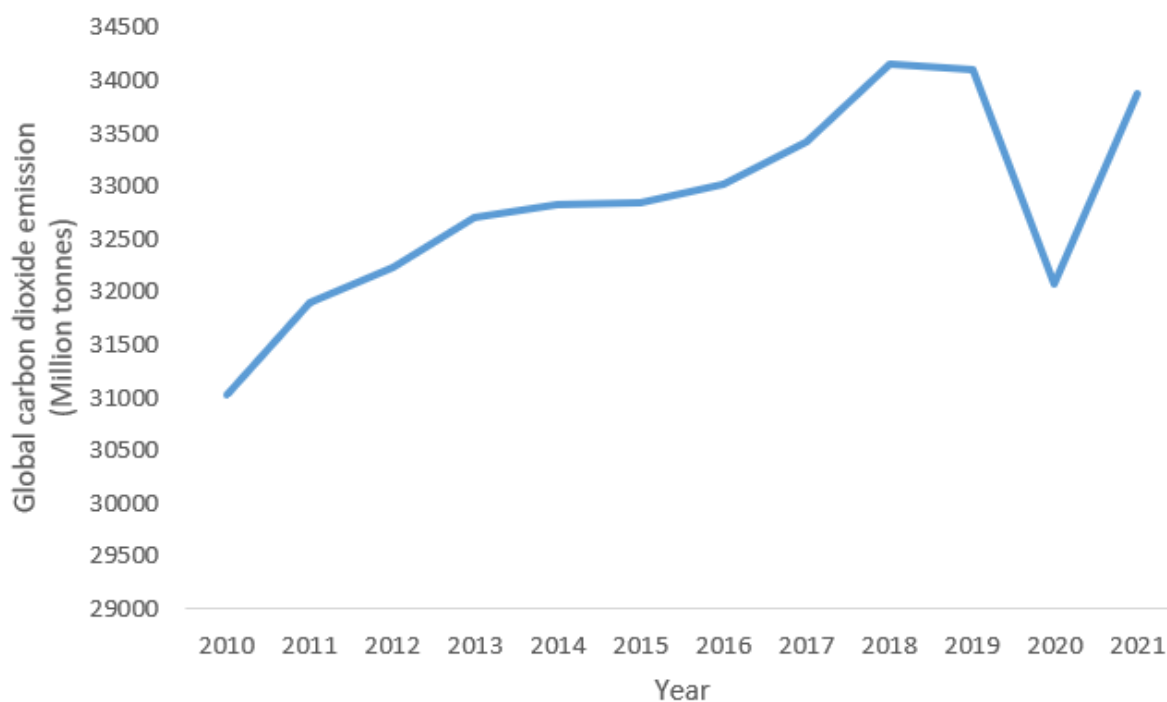


Figure 1.3 Global carbon dioxide emissions from oil, gas and coal combustion adapted from BP ^[1]

Biomass waste covers a wide spectrum, from plants to animal bodies, is a potential energy source to contribute to the solution of CO₂ emission problems, as CO₂ is removed from the atmosphere during the plant photosynthesis process. Therefore, the carbon element in biomass waste will not change the carbon balance in the atmosphere, which means biomass waste is not only a renewable energy source, but also a greenhouse gas (GHG) neutral energy source.^[2]

Based on this advantage, governments have been promoting the use of biomass to generate more energy in the 21st century. Until 2005, the energy generated by biomass in European Union has exceeded the sum of all other renewable energy sources.^[3] And the ratio of energy from biomass in renewable energy in the EU increased to almost 60% in 2019 and this number will continuously increase according to future plan and strategy.^[152] In China, the electricity generated from biomass energy increased from 17.81 MkW in 2018 to 41 MkW in 2022.^[4, 7]

Added-value compounds generated by biomass is another application of biomass waste. As one of the most important added-value compounds, ethanol is requested as the energy source of new energy vehicles in all Chinese market by Chinese government.^[8] The same plan also asked companies to improve their ethanol-generating ability, which reach 11.7 million tons in 2019. USA allowed the E15, a mixed fuel that contains 15% ethanol, which is higher than the normal

ethanol mixed fuel, to be sold from 2018. These cases show that biomass has a large potential market in next several years.

Pyrolysis constitutes a different route for obtaining fuels and chemicals from biomass. Lignocellulosic biomass waste is considered as an ideal feedstock choice as it can be obtained not only from agricultural, but also from forestry residues. However, biomass has some important disadvantages for pyrolysis. For example, high water and oxygen content, complex structure and products, low quality bio-oils. Among these disadvantages, the problem that pyrolysis of biomass and lignin leads to relatively low yields of a poor-quality oil has attracted attention of researchers.

Among its three main components, cellulose, hemicellulose and lignin, the latter has key differences in pyrolysis performance respect to cellulose and hemicellulose.^[9] Lignin is also relatively easy to separate because of its different chemical characteristics, leaving behind cellulose and hemicellulose to be utilised as a source for ethanol and platform chemicals. Therefore, this research will focus on the pyrolysis of lignin separated from the original biomass.

Technologies are being developed that can guide biomass and lignin pyrolysis process to generate specific oil products. Among them, selective catalytic pyrolysis is considered as a potential method to achieve targeted products. Due to its chemical nature, lignin is an interesting source of aromatic building blocks currently derived from the petrochemical industry, such as benzene, toluene and xylenes (BTX).

In pyrolysis processes, when target products are small molecules of oil or gas, hydrogen is widely used to prevent cracking products to re-condense to char by stopping C-C bond formation and stabilising cracking products. Many previous studies directly introduce hydrogen into a biomass or lignin cracking reactor or generate hydrogen in the reactor to produce oil and decrease the generation of char.^[5, 6, 39]

Methane is a potential source for in-situ hydrogen generation for lignin pyrolysis process. There are several potential ways in which hydrogen from methane can be available to lignin. Introduction of methane could generate hydrogen through steam methane reforming, carbon formation as well as non-oxidative direct methane aromatization (DMA). The latter reaction will generate not only hydrogen, but also BTX and could therefore add to the BTX produced

by lignin project. Hydrogen may also be donated through a free radical mechanism to lignin fragments produced thermally. Both reactions will happen under methane simultaneous pyrolysis. According to published research, during methane and lignin simultaneous pyrolysis tends to generate less char and is more sensitive to catalysts than cellulose and hemicellulose^[84], which adds to the drive for operating the process with lignin rather than the whole biomass. A previous study showed that activated methane is beneficial to C-C bond breaking and lignin cracking, increasing oil yields.^[89] During generate H₂, the carbon in CH₄, which may also from fossil or other biomass and animal according to how the CH₄ was collected, was fixed in deposit carbon or BTX which will not enter the atmosphere. That can further reduce the greenhouse gas emissions. And this new source of solid carbon can also reduce the CO₂ that may release into the atmosphere.

1.2 Aim and Objectives

The aim of this study is to develop a process where CH₄ and lignin are co-pyrolysed for the production of BTX. The objectives are the following:

- (1) To modify an existing laboratory-scale fluidized bed reactor to operate the CH₄/lignin pyrolysis process.
- (2) To develop a pre-treatment process to transform lignin into a form that can be smoothly fed to the fluidized bed reactor without blockages.
- (3) To study the influence of temperature, feeding rates, pressure and total gas flow rate on product yields and selectivities in DMA, lignin pyrolysis as well as CH₄/lignin simultaneous pyrolysis.
- (4) To investigate the performance of different catalysts in DMA, and CH₄/lignin co-feeding experiments.
- (5) To examine the effect of placing a catalytic fixed bed downstream from the fluidised bed and analyse the effect of this two-stage reactor system on performance.
- (6) To make recommendations on future works direction of laboratory-scale lignin pyrolysis facilities and the commercial catalyst used in the CH₄ and lignin pyrolysis.

1.3 Thesis Outline

This study is presented over seven chapters. The subsequent chapters are outlined below.

Chapter 2 introduces a literature review focusing on previous studies on CH₄ and lignin thermal chemistry and catalysts used in lignin pyrolysis.

Chapter 3 illustrates the experimental details, including materials and setup used in this work, as well as analytical techniques and procedures. Repeatability, experimental error, and mass balances are also presented in this chapter.

Chapter 4 discusses the experimental results of experiments with CH₄ only under different operating conditions.

Chapters 5 and 6 describe the experimental results of CH₄ and lignin co-feeding experiments.

Chapter 5 focuses on variation of experimental conditions and Chapter 6 on catalyst screening and performance, including the in-situ (in the fluidised bed) and ex-situ (operated as a two-stage system with a downstream fixed bed) catalytic experiments.

Chapter 7 summarises the whole project and gives recommendations for future work.

Chapter 2. Literature Review

The large fossil fuel consumption in energy and petrochemical industry and its increasingly scarce reserves make finding alternative sources for chemical become an important research topic.^[10] As an easy to obtain material, biomass is considered as an attractive feedstock.^[11]

2.1 Biomass

The main constituents of biomass are three: cellulose, hemicellulose, and lignin. Their monomers mainly contain five and six carbon polymers^[11]. They have been widely used in industrial applications^[12] for their simple structure and relatively superior thermo-chemical characteristics. Lignin is often regarded as a waste in most of the biorefining process (gasification, pyrolysis etc.). In industry, lignin is used to directly generate heat and power^[13]. However, lignin has some unique characteristics during biorefining processes, especially for pyrolysis. For example, a pyrolysis experiment done by Yang^[14] shows that cellulose and hemicellulose are not sensitive to catalytic selectivity, but lignin did have sensitivity when using different catalysts, which is an important characteristic for the research on this topic.

2.2 Lignin

2.2.1 Lignin Structure

Lignin is one of the main components of biomass. The ratio of lignin in biomass depends on the kind of biomass. For instance, the shell of some nuts usually has a high lignin fraction, around 51.3%, while tree leaves are absolutely lignin-free^[15]. Previous research shows that lignin acts like a bond between cellulose, hemicellulose and the cell wall. Hemicellulose coat cellulose microfibrils and lignin fills the empty place^[16].

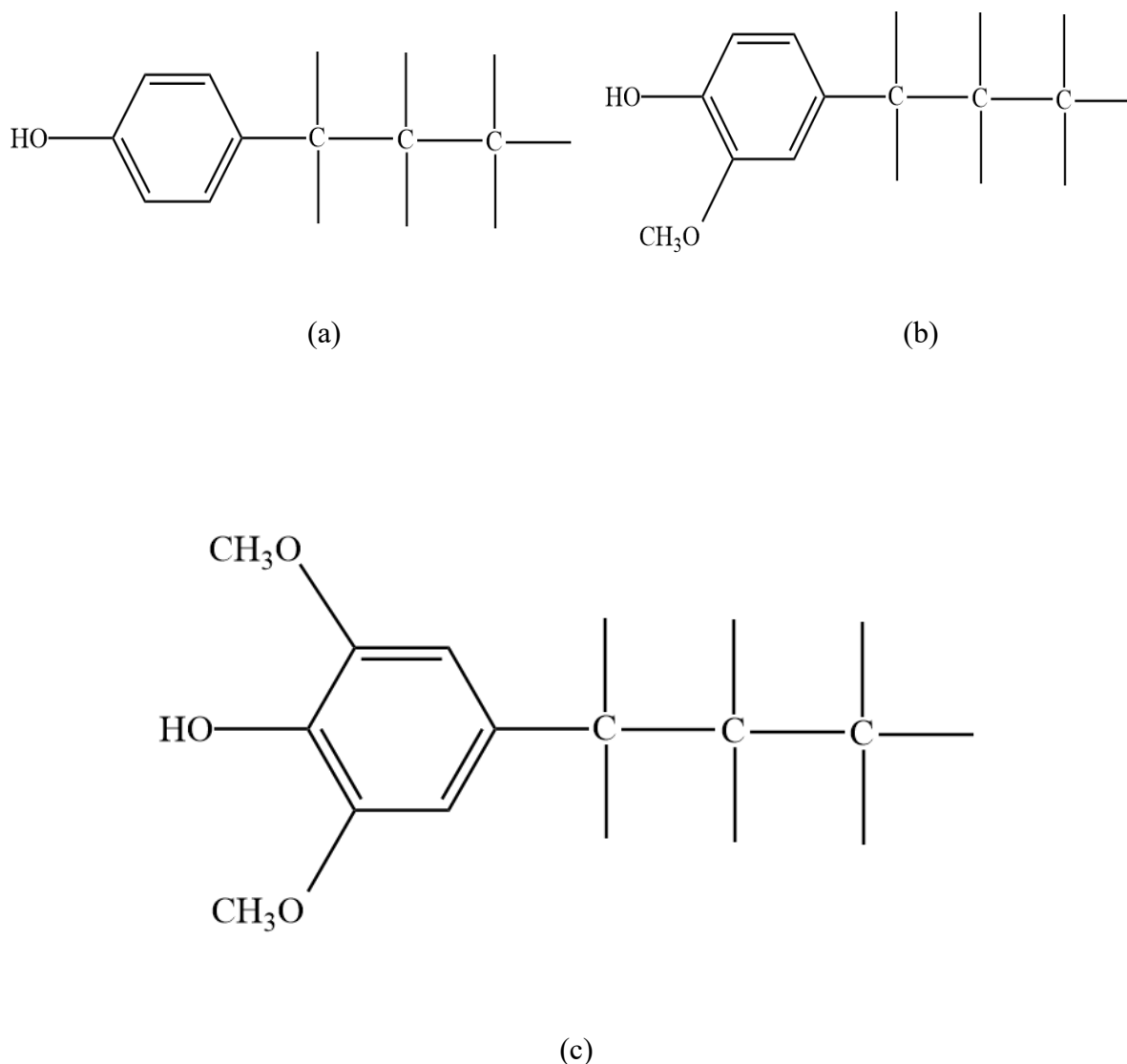


Figure 2.1 Structure units of lignin: (a) coumaryl, (b) guaiacyl, (c) syringyl.

As an amorphous polymer, lignin is composed of 3 phenylpropane monomers, as shown in Figure 2.1, so called coumaryl (p-hydroxyphenyl (H)), coniferyl (guaiacyl (G)), and sinapyl alcohols (syringyl (S)), which may contain respectively 0, 1, 2 methoxyl groups^[17]. The exact structure of lignin is different according to the lignin source which made it difficult to accurately detected all lignin structure in previous study^[18]. However, the major linkages between lignin monomers have been found as shown in Figure 2.2. The main link between lignin monomers is ether, representing around two-thirds of total linkage in native lignin, with C-C bonds as another contributor.

As the most widely distributed phenolic polymer, lignin can be an interesting source of aromatics, which are valuable chemicals used for various industrial synthesis routes, and

contribute to substitution of petrochemicals. [19]

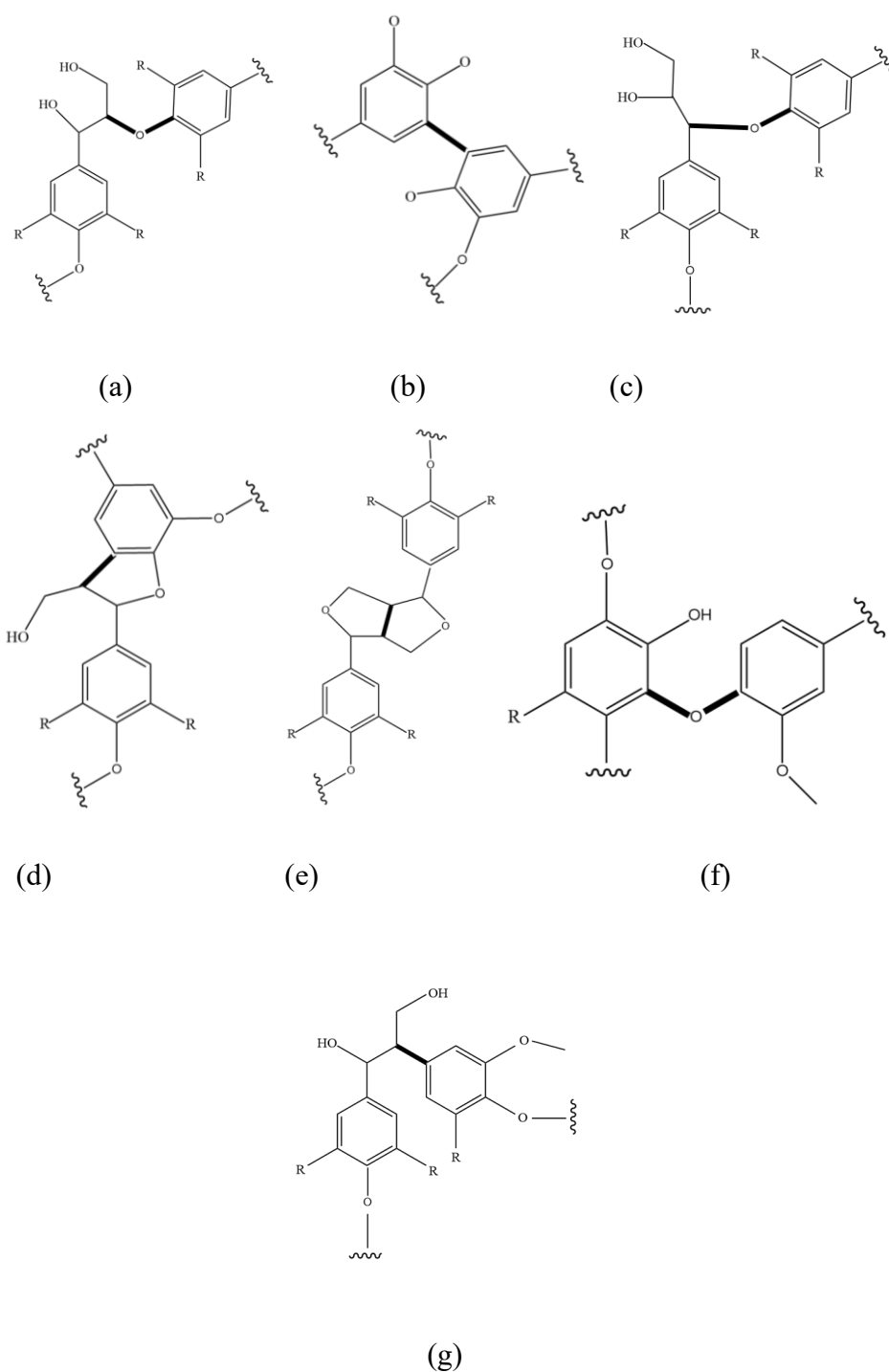


Figure 2.2 Major linkages found in lignin polymer: (a) β -O-4, (b) 5-5, (c) α -O-4, (d) β -5, (e) β - β , (f) 4-O-5, and (g) β -1 [18]

2.2.2 Kinds of Lignin and Lignin Pre-treatment

In laboratory scale experiment, raw lignin which usually generated by some other chemical

process, for example paper refiners process, is not suitable to be used directly for its high sulphur containing rate. High sulphur containing lignin will generate some products contains sulphur, for example SO_2 , H_2S , which might deactivate catalyst.^[18] This raw lignin has disadvantages like complex structure, low purity and harmful compounds contained. Different pre-treatment methods were designed to obtain high-purity lignin. Three kinds of lignin, classified according to the pre-treatment methods, are most widely used in industry and laboratory: Kraft lignin, sulphite lignin and organosolv lignin ^[20]. For different biomass sources, the pre-treatment chosen to isolate lignin will likely differ as the linkage between units can be significantly different ^[21].

Based on experimental requirements, the kind of lignin to be used as feedstock should be chosen carefully. Main characteristics that should be considered are pH, particle size ^[22], surface structure and chemical structure ^[23]. The particle size of lignin after pre-treatment process is usually small, which may cause some problems to feeding systems.

In the next section, three traditional lignin isolating processes and their lignin product will be illustrated. Furthermore, the advantages and disadvantages of each will also be explained and serve as basis to finally choose the lignin to be used in the experimental part of this project.

2.2.2.1 Kraft Lignin

A dominant role is played by Kraft lignin for chemical pulping process in the world. In the United States, more than twenty million metric tons (after air drying) of lignin were produced through this method in 1995 ^[24]. The Kraft method is relatively simple, and usually appears as part of a pulping process.

The conventional Kraft cooking process makes white liquor react with wood chips. The main contents of white liquor are NaOH and sodium sulphide, which makes the environment of Kraft lignin after reaction have a very large potential pH value range, usually between 2 to 12 depending on the type of sulphite used ^[25]. This reaction between white liquor and wood chips happens in a high pressure vessel, so called digester. Cooking temperature is about 170 °C and the reaction time is usually 2 hours. After extraction, relatively high-purity lignin can be gotten. This lignin should be further purified in factory if it was used in laboratory. ^[26] Dissolved Kraft

lignin has more C-C bonds and free phenolic groups than native lignin due to the harsh conditions applied in Kraft pulping ^[27].

Kraft lignins from different suppliers have very different characteristics, including the pH value and sulphur content. Kraft lignin supplied by Sigma-Aldrich Merck (CAS number 8068-05-1) is weakly acidic, with pH of 6.5 at 25 °C and have both low-sulphur and normal sulphur version supplied in stock. Its most important advantage is that this lignin has a large particle shape rather than small particle size powder shape. The main disadvantage of Kraft lignin for using in experiments is its relatively complex structure and moderate molecular size. Lignin generated from this process has many different units with varying structural features, which will increase the difficult of analyses.

2.2.2.2 Sulphite Lignin (Lignosulfonate Process)

Lignosulfonate process is considered a potential way to generate lignin-rich black liquor from forest wood ^[28]. Sulfite lignin can be generated from sulfite pulping process, which has a typical pH ranges from 1 to 5. ^[153] In sulfite pulping process, sulfonation and hydrolysis are the main reactions. During this process, the hydroxyl group is lost and quinone methide intermediate is formed (hydrolysis), and then the sulfite ions in solutions add to the intermediate structure to generate acid units (sulfonation). ^[154, 155]

Sulphite lignin can be generated in some other alternative methods: sulfuric acid treatment, nitration, hydroxypropyl sulfonation, and even sulfonated from kraft lignin. ^[154] In some special cases sulphite lignin was considered as an ideal lignin source, for example, as oil drilling additives and colloidal suspensions stabilizers. ^[153,154]

However, the sulphite lignin has significant disadvantages in lignin cracking. Most of the sulphite pulping delignification processes is accompanied by ether bonds conversion to carbon to carbon bonds. That makes the lignin obtained from lignosulfonate process have very complex and large chemical structure, as shown in Figure 2.3, which is unfavourable for analysing. This carbon to carbon bonds may need more energy to break and may lead to additional fragmentation to happen. Another disadvantage of sulphite lignin is its low purity. Lignosulfonates usually contain by-products of pulp production and recovery, which makes

lignosulfonates lignin have a wide molecular weight range.^[11,29,30] High-sulphur lignins will generate SO₂ and H₂S, among other sulphur-containing products, which might deactivate the catalyst.^[18] And the sulphite lignin is water soluble, that made it very hard to be separated from char after lignin cracking experiment.^[154] This water soluble property can also made sulphite lignin to adsorb steam exist in air which can further increase the difficulty of pre-treatment or feeding during experiment.

Sulphite lignin currently lacks research on its properties and structure. These disadvantages make it an unsuitable choice for lignin refining experiment. A comparison of sulphite lignin and Kraft lignin is shown in Table 2.1.

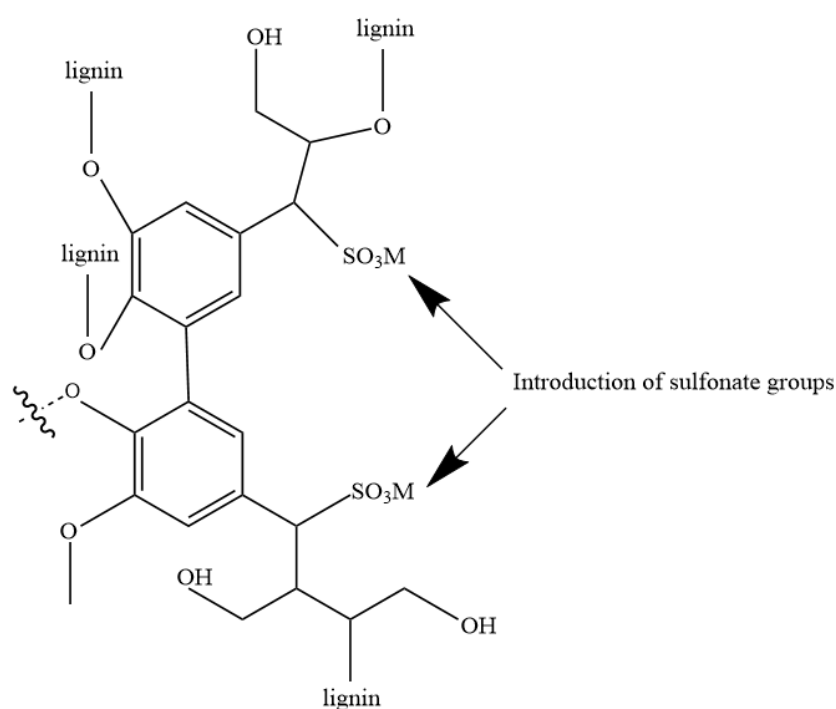


Figure 2.3 Model structure of lignosulfonate lignin ^[25]

Table 2.1 Properties of Kraft and Lignosulfonates Lignin ^{[25][156]}

Property	Kraft lignin	Lignosulfonates
Molecular weight	2000-3000	20000-50000
Organic sulfur, %	1-1.5	4-8
Color	Dark brown	Light brown
Sulfur amount, wt. %	1.0-3.0	3.5-8.0

2.2.2.3 Organosolv Lignin

Organosolv lignin has a relatively simple and clear structure (as shown in Figure 2.4) and is considered as an ideal source for depolymerization and dissolution process.^[31,32] After organosolv pre-treatment, the three main components of biomass can be efficiently fractionated in one fell swoop. In organosolv pre-treatment process, many solvents can be chosen, for example, aliphatic alcohols, ketones, ethanol and water mixtures.^[33,34] That means the organic solvents of organosolv pre-treatment are very easy to obtain and recover. Organosolv pre-treatment can also directly generate solid lignin after isolation, and the by-product of this process is carbohydrates as syrup. This by-product can be used as other process feedstock.^[35,36,37] Another advantage is that, with the help of catalysts, the organosolv process can be done under 100-250 °C. When using organic peracid pre-treatment, organosolv lignin can be produced under room temperature.^[38] Furthermore, the pH value of organosolv lignin can be well designed. If the pre-treatment is done under relatively high temperature (185 to 210 °C), the pre-treatment process will not need acid addition.

However, the organosolv lignin is usually present as clay-like powder shape. The small powder has a high viscosity and is prone to agglomeration. This characteristic makes organosolv lignin hard to pass through tubes that have small inner diameter. The organosolv lignin also has a very low pyrolysis beginning point. According to Wild's research (2012),^[39] the organosolv lignin can begin to crack at 200 °C. The preliminary oil generated under this temperature can further increase the risk of tube blockage in the feeding system of the reactors employed. Whether to

choose organosolv lignin as a feedstock needs further investigation based on the different feeding systems.

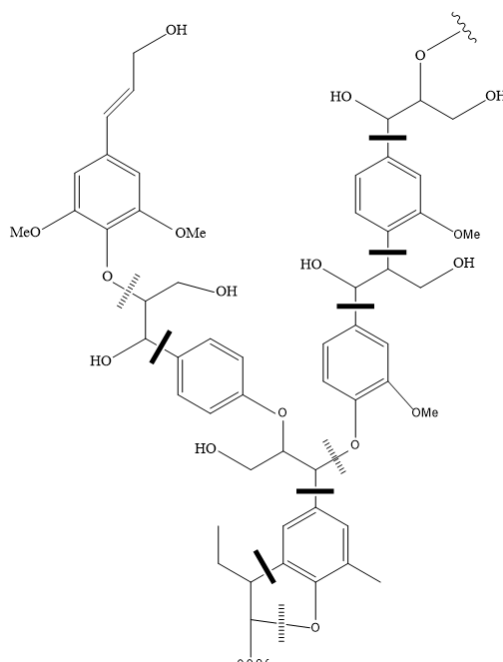


Figure 2.4 Structure of organosolv lignin ^[40]

2.3 Pyrolysis

2.3.1 Pyrolysis Principles

Pyrolysis is a process that involves thermochemical decomposition of a feedstock, usually biomass or coal, into some valuable products. The conversion mechanism of pyrolysis has been well researched. Decarboxylation, decarboxylation, hydrocracking, hydrodeoxygenation and hydrogenation of the biomass components are the main reaction pathways.

As both of them belong to thermal cracking process, pyrolysis has a significant difference with gasification. This difference is that in pyrolysis process, no gasification medium will be present in the system. When pyrolysis experimental systems have steam or other oxygen sources injection and temperature is increased, gasification will happen.^[41] Pyrolysis and gasification processes can convert low value feedstocks into marketable fuels (gas products) and chemicals (oil products).^[42]

Pyrolysis of biomass is typically carried out at a relatively low temperature. According to former research, this temperature is around 300 to 650 °C while gasification may happen at 800 to 1000 °C. The pyrolysis process involves heating the feedstock in an atmosphere free from oxygen (as well as any other reactive gases) to the maximum or target temperature and holding at this temperature for a certain time. ^[43]

Pyrolysis primary products are permanent and condensable gases and char. The condensable gases may then experience further cracking to generate some more non-condensable gases, liquid and char. The pyrolysis process can be expressed as a generic reaction like Equation 2.1.



The main liquid and gas products of biomass pyrolysis are shown in Figure 2.5.

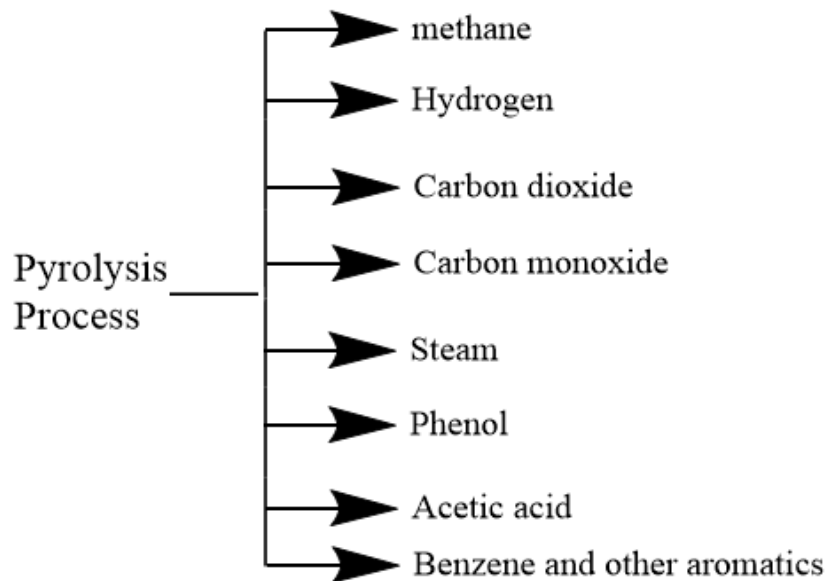


Figure 2.5 Products of biomass Pyrolysis process (Reproduced from Basu, 2010) ^[42]

2.3.2 Types of Pyrolysis

Pyrolysis can be broadly divided between slow and fast. This definition is based on the heating rate. If heating time is much longer than reaction time, the pyrolysis will be slow. ^[44]

Slow pyrolysis is primary used as a method to promote the generation of char. The residence

time is usually of the order of minutes and the final temperature not too high. This kind of pyrolysis can be further divided into carbonization and conventional, as shown in Table 2.2. By contrast, fast pyrolysis has a short residence time, typically of seconds or shorter. Fast pyrolysis is an ideal way to generate bio-oil and gas and can be further divided into two types: flash and ultra-rapid. Among these processes, the carbonization process is the slowest process and the ultra-rapid is the fastest (Table 2.2).

Table 2.2 Characteristics of some pyrolysis processes (Reproduced from Basu, 2010)^[42]

Pyrolysis Process	Residence Time	Heating Rate	Final Temperature (°C)	Products
Carbonization	Days	Very low	400	Charcoal
Conventional	5-30 min	Low	600	Char, bio-oil, gas
Fast	< 2 s	Very high	~500	Bio-oil
Flash	< 1 s	High	<650	Bio-oil, chemicals, gas
Ultra-rapid	< 0.5 s	Very high	~1000	Chemicals, gas
Vacuum	2~30 s	Medium	400	Bio-oil
Hydropyrolysis	< 10 s	High	<500	Bio-oil
Methano-pyrolysis	< 10 s	High	>700	Chemicals

Traditional pyrolysis does not usually contain medium (air or water etc.) but a reactive atmosphere involving the use of water (hydrous pyrolysis) or hydrogen (hydorpyrolysis) has been employed. Hydropyrolysis can improve the volatile yield of reactions, including low molecular weight gas ^[45]. Hydrous pyrolysis (also called as hydrothermal liquefaction, HTL), which uses high temperature water to crack the biomass has been used commercially. The main

products of this process are fuel, fertilizer and bio-oil.^[46] The optimal condition of HTL was at 200 to 400 °C and 10 to 25 Mpa. This condition is approaching to the critical point of water which can change several properties of water significantly and made water can fast and efficiently involved in reaction. This subcritical water can also play a leading role in heat transfer.^[157]

Hydrothermal Carbonization (HTC) is another thermal cracking technology that involved water as reaction medium. This process can be operated in a closure system under 180 to 250 °C. By using HTC, the wet biomass or lignin did not need to be dried before experiment. And the char generated by HTC tends to have a high thermal stability carbon content in its char product.^[158]

2.3.3 Lignin Pyrolysis

Lignin depolymerization is a promising route to obtain aromatics from biomass. Lignin pyrolysis has been applied as a depolymerization strategy, converting lignin macromolecules into bio-oils. ^[47, 48, 49, 50] The bio-oils contain benzene, toluene, xylene (BTX) and other aromatics, including phenols, as the main components.^[51 52] However, lignin pyrolysis under inert gas atmosphere still tends to generate significant char yields, and the bio-oil contains large quantities of oxygenated and polyaromatic compounds.^[53]

2.3.4 Gasification

Gasification takes place under high temperature and in a partial oxidation atmosphere, where molecular oxygen is involved. Compared to pyrolysis, gasification tends to generate more high valuable gases. Some methane is generated in gasification and it can be consumed in the steam methane reforming reaction, which is shown in Table 2.3 along with gasification major reactions.

Table 2.3 Major gasification reactions (Reproduced from Higman, 2008)^[54]

Reaction type	Reaction	$\Delta H, \text{MJ kmol}^{-1}$
Combustion reactions	$C + 0.5O_2 \rightarrow CO$	-111
	$CO + 0.5O_2 \rightarrow CO_2$	-283
	$H_2 + 0.5O_2 \rightarrow H_2O$	-242
Boudouard reaction	$C + CO_2 \leftrightarrow 2CO$	+172
Water gas reaction	$C + H_2O \leftrightarrow CO + H_2$	+131
Methanation reaction	$C + 2H_2 \leftrightarrow CH_4$	-75
CO shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$	-41
Steam methane reforming reaction	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	+206

2.4 Pyrolysis Systems

2.4.1 Fixed-bed Pyrolyzer

Fixed bed pyrolyzers (FBP) are the oldest type of pyrolysis system and still used in current research. FBP operate in batch mode. This type of reactor has the advantages of being easy to use and having low blockage risk. However, fixed bed reactors tend to have a limited oil (especially light oil) and gas yield in pyrolysis.^[58]

2.4.2 Bubbling Fluidized Bed

This type of reactor has been used in the chemical processing field for over 50 years. In bubbling fluidized reactor, biomass is fed as small particles (2-6mm) into a bed consisting of hot sand and/or catalysts. The bed is usually fluidized by an inert gas or a mixture of reactive

and inert gases. As the solids are fluidized, their residence time should be much longer than the gas.^[55]

Bubbling fluidized bed reactors provide a high heat transfer rate. When the appropriate size of bed fluidizing media is rightly chosen, the gas residence time can be controlled to allow fast pyrolysis to happen.^[56]

According to previous research,^[150] 500 to 550 °C and 0.5 s residence time will provide the highest yield of oil in bubbling fluidized beds. This limits the feedstock particle size as large particle sizes may generate some by-products that are too big to flow out and can block the system. This type of reactor is also hard for catalyst recovery and the catalytic effectiveness is relatively low.

2.4.3 Circulating Fluidized Bed

Circulating fluidized bed (CFB) has a similar working principle to the bubbling fluidized bed reactor, as well as high heat transfer rate and short gas residence time. However, the CFB has a much larger biomass throughput because the superficial gas velocity is higher than in bubbling fluidized bed reactors as the particles can be entrained in the gas. Under this situation, the mixture in CFB will be better and the particle size distribution that can suit this type of reactor is even smaller than for bubbling beds. The whole reactor is operated in a special hydrodynamic regime which is also called fast bed.

This reactor has its advantages. First, it can heat the feedstock at an extremely fast rate. Second, the oil yield and generation rate are very high as a consequence. In Hulet's experiment, the liquid yield reached 83% for a heating rate of 1000 °C s⁻¹.^[57] However, its disadvantage is that feedstock particle size must be controlled within a small range.

2.4.4 Rotating-cone Pyrolyzer

The rotating-cone pyrolyzer is a rotating bowl-like reactor in which the solids are fed into the bottom of the cone with heat carrier particles. This cone will rotate at a rate of 360-900 rpm and the particles will be transported upwards along the wall of reactor due to the centrifugal force applied on them. The oil vapor and gases will leave from another tube and the char will

drop into a fluidized bed surrounding it.^[58]

Rotating-cone pyrolyzers have a significant advantage that the heating rate is extremely high for the full mixing. This heating rate can reach 5000 K s^{-1} . The char, which is burnt in the surrounding fluidized bed can provide heat for the reactions. However, this pyrolyzer has a short solid and gas residence time, which limits its experiment applicability. This pyrolyzer does not have carrier gas, which means the effect of gas environment is hard to be tested.^[59]

2.4.5 Other Pyrolyzers

Many other pyrolyzers are used in commercial or experimental setups, some of which are shown in Table 2.4. Other systems, including plasma, microwave, and solar reactors, are new types of reactor with different advantages and needing more research done on them to provide results.

Table 2.4 Various fast pyrolysis reactor technologies (Reproduced from Sharifzadeh, 2018)^[58]

Reactor type	Advantages	Limitations	Technology readiness
Bubbling fluidized bed	High heat transfer efficiency	Biomass should be in fine particles	Commercialized
Circulating fluidized bed	Relatively easy to scale up	Complex hydrodynamics; similar residence time for char and vapors	Commercialized
Rotating cone	Less carrier gas requirement	Less liquid yield	Under study at laboratory scale
Vacuum pyrolysis	Moderate operating conditions	Slow heat transfer rate	Abandoned in 2002
Screw and auger kilns	Sand or still ball as the heat carrier	Larger particle residence time	Pilot -scale
Microwave pyrolysis	Efficient heating; less restriction on biomass size	Difficult to control	Under study at laboratory scale
Hydropyrolysis	Process intensification	High pressure required	Under study at laboratory scale

2.5 Pyrolysis Products

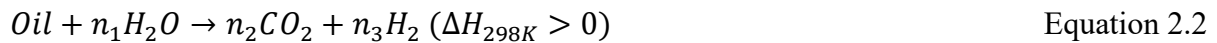
As mentioned above, pyrolysis products are divided into three different kinds: gas, oil (liquid phase which is heavy and condensable organic compound), char (carbonaceous compound)

residue and ash). The lignin fraction in biomass has an important influence on yields of products.^[60] Different biomass will have significant different oil yields.

2.5.1 Gas

In pyrolysis, gas is usually considered as a by-product.^[61] The main gas generated in biomass pyrolysis is syngas.^[62] Some research proved that in flash pyrolysis, the yield of syngas can reach a high level. For instance, 76.64% syngas yield were reported to be achieved in a plasma reactor.^[63]

The most important parameter that has influence over the generation of gas is temperature. When temperature increases, drying will happen first. This includes evaporation of moisture, devolatilization and partial degradation. At the same temperature of devolatilization and degradation start, the generation of oil will begin. This oil and volatile released from a particle may be involved in a series of further secondary reactions.^[64] Oil cracking can be approximately described by the following equation:



Previous experimental results showed that under 900 °C, an increase in temperature will favour the oil decomposition and thermal cracking, leading to increasing gas yields^[65] and decreasing of oil and char yields. When the target product is oil, temperature needs to be controlled to ensure the oil yield is high enough while the reaction rate is not too low.

2.5.2 Oil

Oil generated in pyrolysis is a complex mixture of condensable species, including heteroatomic compounds and mono- and polyaromatic hydrocarbons.^[66] Some studies consider oil as an unwanted/harmful pyrolysis product and aim to reduce oil yields or remove the oil using many different ways.^[67] This is because the oil composition is complex and despite many compounds in it being high added-value and worth to be obtained, the means to improve their yield and separating them are not straightforward. To obtain high added-value light oil from biomass and

lignin, C-C and C-O bonds need to be broken and the resulting radicals stabilized with hydrogen addition.

2.5.2.1 Effect of Temperature

Depending on the feedstock and reactor type, the maximum liquid production by pyrolysis will be obtained between 350 and 710 °C.^[68] At temperatures lower than 350 °C, only limited depolymerization takes place. When the temperature in the range of 350 °C to 500 °C, glycosidic linkages are broken, dehydration begins to happen and sugar units are rearranged and cracked. After the temperature increases to higher than 500 °C, all processes illustrated above happen at the same time. Previous experiments show that the peak of oil yields for lignin is higher than for most whole biomasses.^[68] This study showed that the maximum yields of oil from lignin are obtained at approximately 600 to 650 °C.^[68]

2.5.2.2 Pressure and Volatile Residence Time

Volatile residence time depends on the gas flow rate and will affect several secondary reactions.^[69] A prolonged volatile residence time leads to a decrease in oil yields but volatile residence time shorter than 1 s will affect the biomass decomposition process by causing lignin to have an incomplete depolymerization.^[70]

Pressure significantly affects biomass pyrolysis yields. The higher operating pressure will lead to a higher concentration of volatiles and an increase in the decomposition rate in secondary reactions.^[71] Other study in wire mesh reactor showed a opposite result that high pressure atmosphere can suppresses volatile release.^[151] The influence of pressure to lignin pyrolysis should be further studied.

2.5.2.3 Heating Rate

Heating rate affects the properties of bio-oil, including its water content, which is significantly lower in fast than in slow pyrolysis.^[61] Volatiles from slow pyrolysis are significantly affected by secondary cracking. An increase in heating rate decreases the char and oil yields and increase gas yield.^[72] Previous research also shows that a lower heating rate favours the

generation of small molecules in the liquid.^[67]

2.5.2.4 H₂ Concentration

Lignin pyrolytic depolymerization with a H₂ source can effectively increase the monoaromatic yield.^[73] This has been observed in the hydropyrolysis of corn stover lignin^[74], where the carbon yield of aromatic hydrocarbons was reported to increase from 9.67 C% in helium to 19.23 C% in H₂ atmosphere, and in the introduction of H₂ in the pyrolysis of an organosolv lignin, which showed an increase in the yield of simple phenols, benzene and toluene.^[75]

2.5.3 Char

Char products usually retain approximately 25% of the energy in the feedstock.^[61] These biochars contain organic have not been converted and other residues solid. Char yields depend on biomass/lignin type, temperature, heating rate and particle size of feedstock. Animal litters tend to have higher char yields than plant biomass. The widest application of biochar is made as filter or support. The potential uses in filtration and as support are given by the microscopic surface structure.^[76, 77]

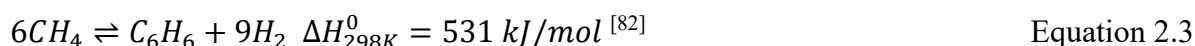
Pyrolysis bio-chars or deposit carbon have usually been considered as low added value products. However, when methane is introduced in the system, the methane cracking can generate carbon nanotubes during the process and remain in the char.^[78] Results reported before show that under pyrolysis-like conditions, with the nickel oxide as catalyst (also a commonly used catalyst for biomass pyrolysis), 99% purity methane can form carbon nanotubes that meet the requirement of industrial applications.^[78] Considering a situation where the methane conversion in simultaneous pyrolysis of biomass and methane is low, carbon nanofibers may be an interesting by-product to convert the excess methane.^[78, 79]

2.6 Direct Methane Aromatization

As illustrated in Section 2.5.2.4, the presence of H₂ in the reactor can help in improving oil yields from lignin pyrolysis. The source of H₂ for lignin depolymerization is important, as H₂ is a relatively expensive gas and at high purity is likely to be under increasing demand as fuel

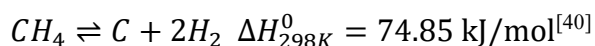
for both transport and stationary applications. These economic considerations together with the reportedly higher reactivity^[80, 81] make the in-situ produced hydrogen an alternative source that is worth investigating. Processes that use coupling of hydrogen production and hydrogenation reactions are appearing in the literature on bio-oil upgrading.^[80] This work focused on the use of CH₄ to generate H₂ simultaneously to the pyrolysis of lignin.

Direct methane aromatization is a reaction to transform CH₄ to H₂ alternative to gasification and methane decomposition into carbon and H₂. By contrast with gasification, instead of CO₂ it produces benzene through Equation 2.3.^[82] The by-products of DMA are long chain alkanes, toluene, ethylbenzene and xylenes as well as other aromatics observed at long reaction times.^[83, 84] The gas products from DMA only contain H₂ and unreacted CH₄, while the oil phase is composed of benzene as the main product, also containing some toluene, ethylbenzene and xylenes (BTEX). These are high-value chemicals widely used in the chemical industries.



The DMA reaction has similar optimum reaction conditions to lignin pyrolysis, and the catalysts used for DMA can also catalyze the process of lignin conversion.^[85, 86] The catalyzed DMA reaction begins to happen at temperatures around 550 °C at atmospheric pressure and the benzene generation is continuous up to 1030 °C.^[87] This range overlaps with the lignin pyrolysis temperatures, typically between 330 °C and 600 °C^[88, 89]. The hypothesis investigated in this work is that hydrogen generated by DMA is available, even as atomic H on the catalyst active sites, to aid in the stabilization of radicals produced by chemical bonds breaking in lignin, to increase yields of BTEX and other small molecules.

CH₄ cracking, also referred in the literature as CH₄ pyrolysis, is shown in Equation 2.4 and can happen in parallel to the DMA reaction. It is favoured by high temperature with the optimal CH₄ cracking temperature varying widely for different catalysts. Ni-based catalysts can enable CH₄ pyrolysis to take place at 500-700 °C, while Fe-based catalysts have an optimal temperature of 700-900 °C and the range for carbon-based catalysts is 800-1000 °C.^[90] The formation of a carbon deposit during CH₄ cracking is also one of the main reasons for catalyst deactivation in lignin pyrolysis.^[91, 92, 93]



Equation 2.4

2.7 Catalyst Used in Pyrolysis

The use of a catalyst has become one of the most important research interests in pyrolysis area.^[94] Among the functions of a catalyst are enhancing cracking of high molecular weight compounds into lighter ones and hydrogenate the products of cracking to make compounds stable in the liquid range. During this process, the breaking of C-C and C-O bonds must happen, and therefore the chosen catalysts should promote this. The activation energy of methane conversion is relatively high, which means catalysts should also have a function to activate methane. Catalysts should be chosen very carefully based on process requirements and target products.

2.7.1 Catalyst Selection

When the target product of biomass pyrolysis is syngas and high added-value oil products, a catalyst that promotes oil cracking will be chosen to meet the requirements of increasing light oil yields in pyrolysis. Three groups of catalysts have been reported to achieve this: dolomite, alkali and nickel catalysts.^[95] Gayubo and co-workers used zeolite ZSM-5 to crack bio-oil (as shown in Figure 2.6). However, ZSM-5 will favour the yield of oil in other conditions, involving lower temperatures.

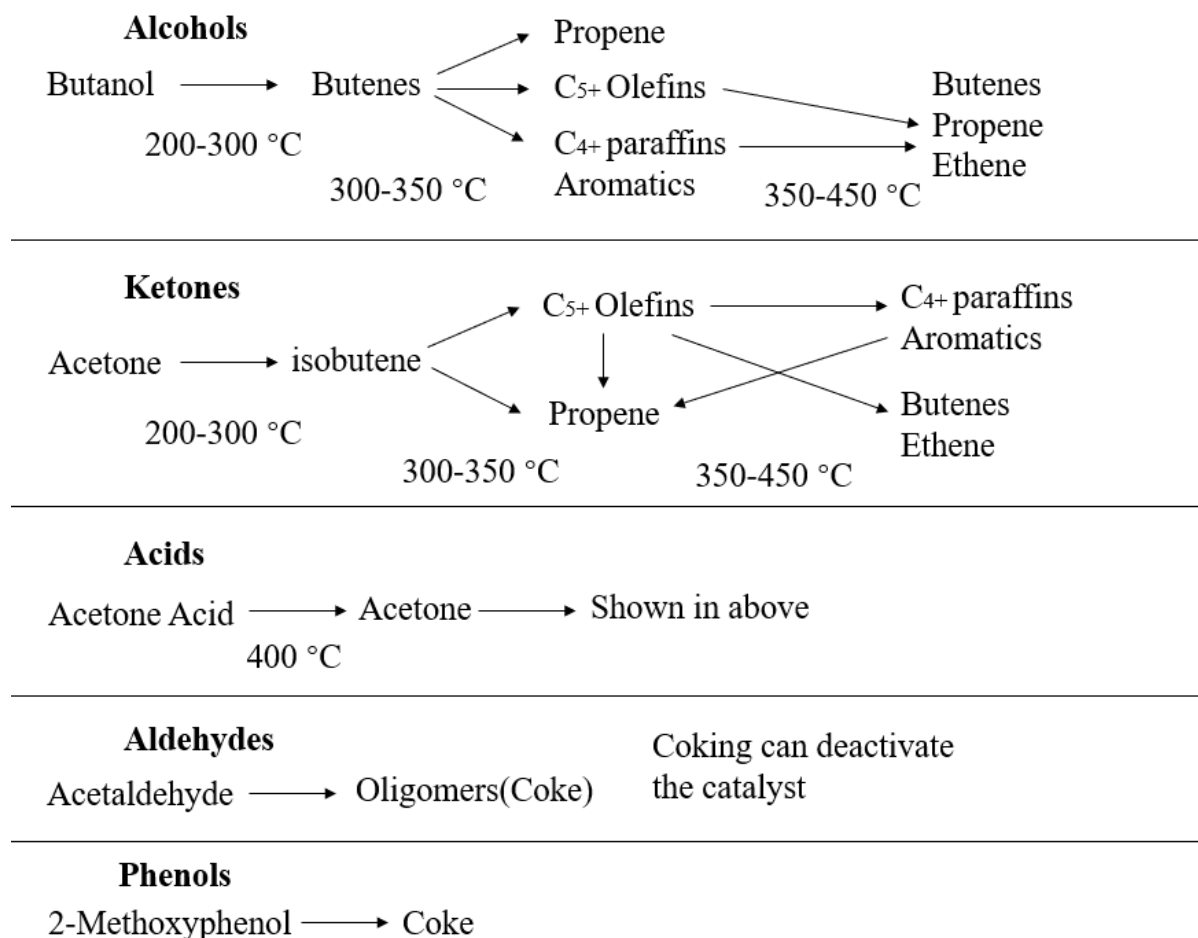


Figure 2.6 The conversion of model bio-oil compounds with ZSM-5. ^[96]

As in this project the target products are BTEX, catalysts that lead to over-cracking of the feedstock should be avoided. Common catalysts used to help oil generation will be illustrated in Section 2.7.2.

2.7.2 Catalysts for Oil Generation

2.7.2.1 Zeolite

Zeolite is the most widely used catalyst in lignin pyrolysis research, including in the scarce work available on methane and lignin simultaneous pyrolysis experiments. ^[89] The reaction path of zeolite-catalyzed lignin pyrolysis is shown in Figure 2.7. ^[89]

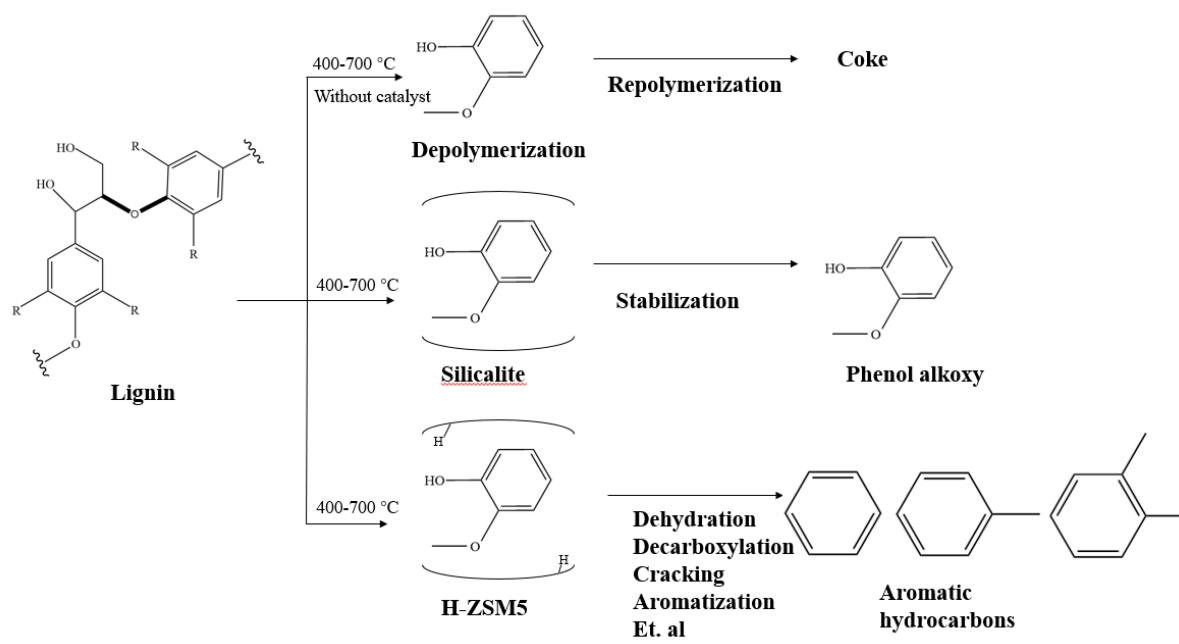


Figure 2.7 Proposed reaction pathway of lignin pyrolysis with and without catalysts. ^[97]

Ma and co-workers listed the pathway of lignin pyrolysis with and without catalysts. They concluded that H-ZSM5 will guide pyrolysis to generate aromatic hydrocarbons. They also found that when the H-ZSM5 content increased, the oil yields improved significantly. It has been reported an oil yield of 58.2% in total products, and the aromatic hydrocarbon yield approaches 40% in all liquid phase products. ^[97]

However, zeolite catalysts have some disadvantages, such as their low hydrothermal stability, which makes them only keep stable for 6h under 150-200 °C in hot water. ^[100] Moreover, the oil yield of zeolite catalytic experiments is relatively low under high temperature.

Ravenelle's result showed that a zeolite-based catalyst has a low oil yield (highest 43% at 550 °C in a fixed bed reactor). There is still a large space for metal and non-metal active sites to be explored. ^[100]

2.7.2.2 Metallic Catalysts

Most catalysts for pyrolysis oil generation experiment in laboratory studies contain metals. ^[23]

Weckhuysen and co-workers tested several different transition metal catalysts in lignin pyrolysis. They found that the general activity order was: Co > Cr > Fe > Ni > Mn >> Cu. ^[101]

Catalysts containing metal active sites have a vital advantage in oil generation from biomass

pyrolysis. Catalyst modifications can also affect the final products of pyrolysis. Work done by Ma shows a potential to link the major products in oil with the kind of catalysts used in the experiment.^[97] Introduction of a second metal as a promotor has been shown to lead to several advantages^[97], comprising increasing activity, modifying selectivity and improving catalyst stability.^[102] This promotion might be caused by hydrogen spill-over or complex metal interactions, which can be divided into five effects: (1) geometric (or ensemble), (2) electronic (or ligand), (3) stabilizing, (4) synergistic, (5) bi-functional. However, there is still a lack of experimental evidence and knowledge regarding the mechanism and specific function of bimetallic catalysts. Research has been done using bimetallic catalysts in hydrocarbon conversion experiments, but these cannot directly be used to explain experiments using biomass. That is because the upgrading strategies for biomass are significantly different to those involving hydrocarbons, and the presence of impurities and greater complexity in the reactants may affect the bimetallic catalyst.^[102]

There is a lack of research on lignin pyrolysis with bimetallic catalysis. Moreover, because of the complex structure of lignin, most research uses model compounds to replace true lignin.^[103, 104, 105] Bimetallic catalysts that contain Mo and Pt have been most studied.^[102] This combination of two metal elements in a catalyst is beneficial to the breaking of C-C and C-O bonds.

2.7.3 In-situ and Ex-situ Catalysts

An in-situ catalyst is one placed in the main pyrolysis reactor (fluidized reactor in this project). In-situ catalysts will catalyze biomass pyrolysis and DMA reaction simultaneously, and it will be closely mixed with biomass or lignin. In-situ catalysts are usually involved in the earlier stage of biomass cracking. In a pyrolysis reactor which has a short residence time, a large catalyst-to-biomass rate is required to ensure the catalytic activity.^[89] However, that is inconvenient in large-scale experiments. Another disadvantage of in-situ catalysts is that the pyrolysis temperature may not be its the optimum working temperature.^[106]

In the case of ex-situ catalysts, they are placed outside the main or first reactor. That provides a way for the catalyst to work under optimized conditions. The reactions catalyzed by ex-situ

catalysts happen between methane, oil and gas products generated by biomass and methane pyrolysis. This catalyst is easier to recover because it will not be mixed with char or bed materials left by pyrolysis.

In methane and biomass simultaneous pyrolysis, the combination of in-situ and ex-situ catalysts led to a higher yield of monoaromatic products than single in-situ catalysts (shown in Table 2.5).

Table 2.5 Comparison of catalytic effect of in-situ and ex-situ catalysts on yields of aromatic HCs, BTEX and Alkylphenols in methane co-feeding biomass gasification, 500° C, 1 bar.^[89]

Run	Catalyst*		Aromatic HCs yields, %	BTEX aromatics yields, %	Alkylphenols yields, %
1	In-situ	HY(30)	3.7	0.2	0.3
	Ex-situ	HZSM-5			
2	In-situ	HY(5.1)	2.8	1.2	0.1
	Ex-situ	HZSM-5			
3	In-situ	NZ	3.2	0.4	1.6
	Ex-situ	HZSM-5			
4	In-situ	HY(5.1)	0.8	0.1	1.9
	Ex-situ	HY(30)			

* All experiments used both in-situ catalyst in first stage reactor and ex-situ catalyst in second stage reactor.

2.8 Methane and Biomass/Lignin Co-feeding Pyrolysis

The major contributions of methane in this pyrolysis system are: (1) as the source of hydrogen,

(2) aiding C-C bond breaking, which activated methane can do, (3) directly generating BTEX by the DMA reaction (Yang, 2016; Iglesia, 2002).^[14, 108] Hydrogen is also beneficial to the cracking process.^[39] Under methane co-feeding pyrolysis, it is hypothesized that hydrogen generated in reactor will increase the oil yield by stabilizing radicals before they continue reacting by regeneration of C-C bonds to form char or further crack to gas. This was illustrated in work by Meier et al. which shows that during lignin or model compound cracking process, higher hydrogen pressure will lead to higher light oil yields.^[109, 110] Hydrogen consumption would change the DMA chemical equilibrium to generate more hydrogen in the reactor.^[54, 98] Under 1 bar, DMA begins to happen at 550 °C and ends at 1030 °C,^[98] while steam reforming and methane decomposition will happen in the range from 550 °C to higher than 900 °C.^[111] Matsumura and co-workers achieved a low reaction temperature for steam reforming of methane using nickel catalysts.^[112] Zeolite is the most widely used catalyst for DMA, but zeolite will begin to deactivate under a low temperature, less than 300 °C, when steam is introduced in reactor. MoO_x is another catalyst investigated in DMA reaction, and it has been shown that it can help to break C-H bonds and catalyze the DMA reaction well.^[98] As shown in Figure 2.8, the DMA process competes with carbon formation on the catalyst. Molybdenum oxide introduced on a zeolite catalyst is also believed to be active for C-H bond breaking process. This characteristic will benefit oligomerization and cyclization reactions to form aromatics.^[99]



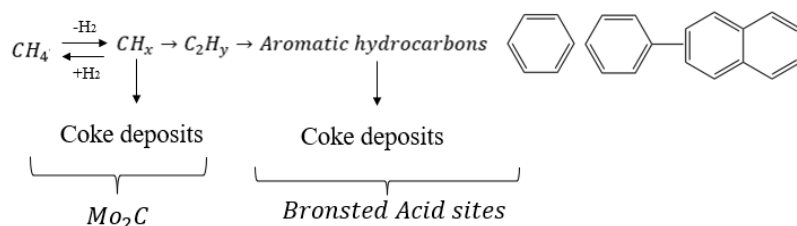


Figure 2.8 DMA reaction pathway ^[98]

Nickel and MoO_x have been used in lignin and methane simultaneous pyrolysis experiments. Under 600 °C and without steam, the results show that nickel has a better oil generation performance than MoO_x .^[89]

Introducing methane into biomass pyrolysis to generate useful oil, especially the BTEX, is a novel process on which the information in the literature is very limited. The first research on this process was done by Steinberg and co-workers in 1986, who found that methane co-feeding with wood pyrolysis led to higher yields of ethylene, benzene and CO under 1000 °C and 1.38 bar.^[113] Without catalyst, the ethylene yield obtained by methane feeding flash pyrolysis is 2.3 times than nitrogen or helium feeding.

After this remarkable research, there was a long time when nearly no one focused on this reaction, but in the last 5 years research on methane and biomass simultaneous pyrolysis intensified, although not much has been published. In the following paragraphs, current research and problems waiting to be solved will be illustrated.

In 2015, Xiao used solid waste (mixture of sawdust, canola straw, pita, bread, newspaper, sludge) as feedstock co-fed with 60% methane and 40% CO_2 to do the pyrolysis with the aid of different zeolite-based catalysts to compare catalytic effects. The highest oil yield (15.25 ± 0.16 %) was obtained from pure sawdust as feedstock, 400-600 °C, 1 bar with 1% Ag-5% Zn/ZSM-5 as catalyst. They found that dispersed welled Zn and Ag species is a good way to increase the catalytic performance of zeolite-based catalysts.^[114]

In 2018, Dutta pointed out a high reaction temperature needed to generate benzene by the DMA reaction (650-700 °C for atmospheric pressure and gallium nitride as catalyst). This research also showed that methane conversion was not directly proportional to the catalyst mass.^[87]

In 2016, Yang and co-workers did very detailed research on different catalysts for methane and cellulose, hemicellulose and lignin simultaneous pyrolysis.^[14] In 2017, this group did another

study on simultaneous pyrolysis of methane and torrefied biomass (raw switchgrass) with HZSM-5 as catalyst. The most important highlight of this research is that it tested the content of all main compounds and their results on lignin (as shown in Table 2.6).^[107]

Table 2.6 Aromatic product selectivity in catalyzed decomposition of lignin in the presence of HZSM-5 supported catalysts under methane atmosphere at reaction temperature of 700 °C^[107]

Catalyst	Polyaromatics (%)	Benzene derivatives	Xylene	Ethylbenzene	Toluene	Benzene
MO ₂ C/HZSM-5	21.3	12.0	20.5	2.2	27.0	17.0
MoO ₃ /HZSM-5	15.6	12.2	20.6	2.7	29.0	19.8
MoAg/HZSM-5	17.5	10.5	15.6	1.9	27.6	27.0
HZSM-5	25.4	9.6	18.8	1.7	26.8	17.7

In Table 2.5 and Table 2.6, we can find that these different catalysts led methane simultaneous pyrolysis to obtain different major products. For example, HZSM-5 promoted reactions that favour polyaromatics to become the main product in oil. MoAg increases the yields of benzene and makes it the main product. Some other relationships between kind of catalyst and main products in oil need to be explored as they will be helpful to increase selectivity towards BTEX. However, a significant problem is that results from methane and helium experiments have not led to large differences. Finding ways to increase methane conversion is an important focus of this project.

Chapter 3. Experimental

3.1 Introduction

This chapter describes the materials used in experiments, the experimental set up and its commissioning, experimental procedures, analytical methods and error analysis.

3.2 Materials

DI water was used as source of steam. N₂ (99.998% purity), H₂ (99.99% purity), CH₄ (99.99% purity), air, and two calibration gas mixtures (1% CH₄, 15% CO, 15% CO₂, 10% H₂, balance in 99.99% purity N₂) for online analysers calibration and (1% n-butane, 1% propylene, 20% CO₂, 10% CH₄, 1% propane, 1% ethane, 20% CO, 20% H₂ balance in He) for calibration of gas chromatography with a thermal conductivity detector (GC-TCD). The supplier of all compressed gases illustrated above is BOC Ltd. Chloroform used as solvent was supplied by Sigma Aldrich. The bed material of the fluidized bed reactor was commercial sea sand (purified by acid and calcined) from Sigma-Aldrich. Commercial catalysts used in this study was from Harshaw Catalysts Industry, and the in-house developed catalyst were prepared by Dr. Guanming Yuan and Mr. Jiaxian Luo. The detail information of these catalysts is given in Chapter 4, 6 and Appendix 5.

Low sulfonate kraft lignin used in formal experiments was supplied by Sigma-Aldrich. The elemental composition of one kraft lignin from China used in agglomeration analysis was also tested. The elemental analyses of Kraft lignin after drying and pretreatment are given in Table 3.1.

Table 3.1 Elemental analysis of Kraft lignin feedstock as dried and pre-oxidated basis.

Feedstock	N (%)	C (%)	H (%)	S (%)	O ¹ (%)
Dried Sigma-Aldrich lignin	1.03	52.62	5.03	2.12	39.20
Pre-oxidated Sigma-Aldrich lignin ²	1.43	57.04	4.57	2.06	34.90
Torrefied Sigma-Aldrich lignin	1.11	57.86	5.24	2.13	33.66
Dried CN lignin	5.83	28.69	4.04	4.15	57.33
Pre-oxidated CN lignin	5.87	28.85	3.48	4.32	57.48
Torrefied CN lignin	6.03	28.92	3.97	4.25	56.83

¹ by difference

² Pre-oxidation process illustrate in Section 3.4.3

A representative structure of Sigma-Aldrich low sulfonate KL is shown in Figure 3.1. In this lignin monomer, all methoxy, oxyhydryl and methyl group can be found on benzene ring.

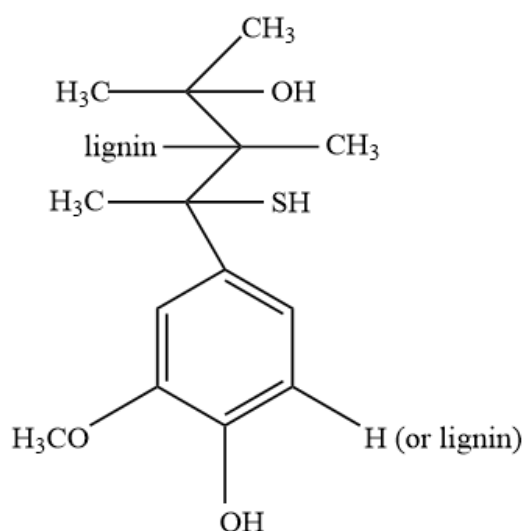


Figure 3.1 Sigma-Aldrich Kraft lignin structure^[148]

3.3 Reaction Experimental Setup

The reactor setup consists of three main parts: a feeding section, including a gas supply system, a steam generator and the solid feeding system; the reactor itself, consisting of an existing laboratory-scale high pressure fluidized reactor with the option of installing downstream a fixed bed reactor for combined in-situ and ex-situ catalyst experiments (Chapter 6); and gas product conditioning and analysis, which comprises a trap to condense any liquids, a gas meter and a burner to flame the output gas. A small slipstream of product gas was sent to online gas analysers. Each of these sections will be described separately below. The process flow sheet is given in Figure 3.2.

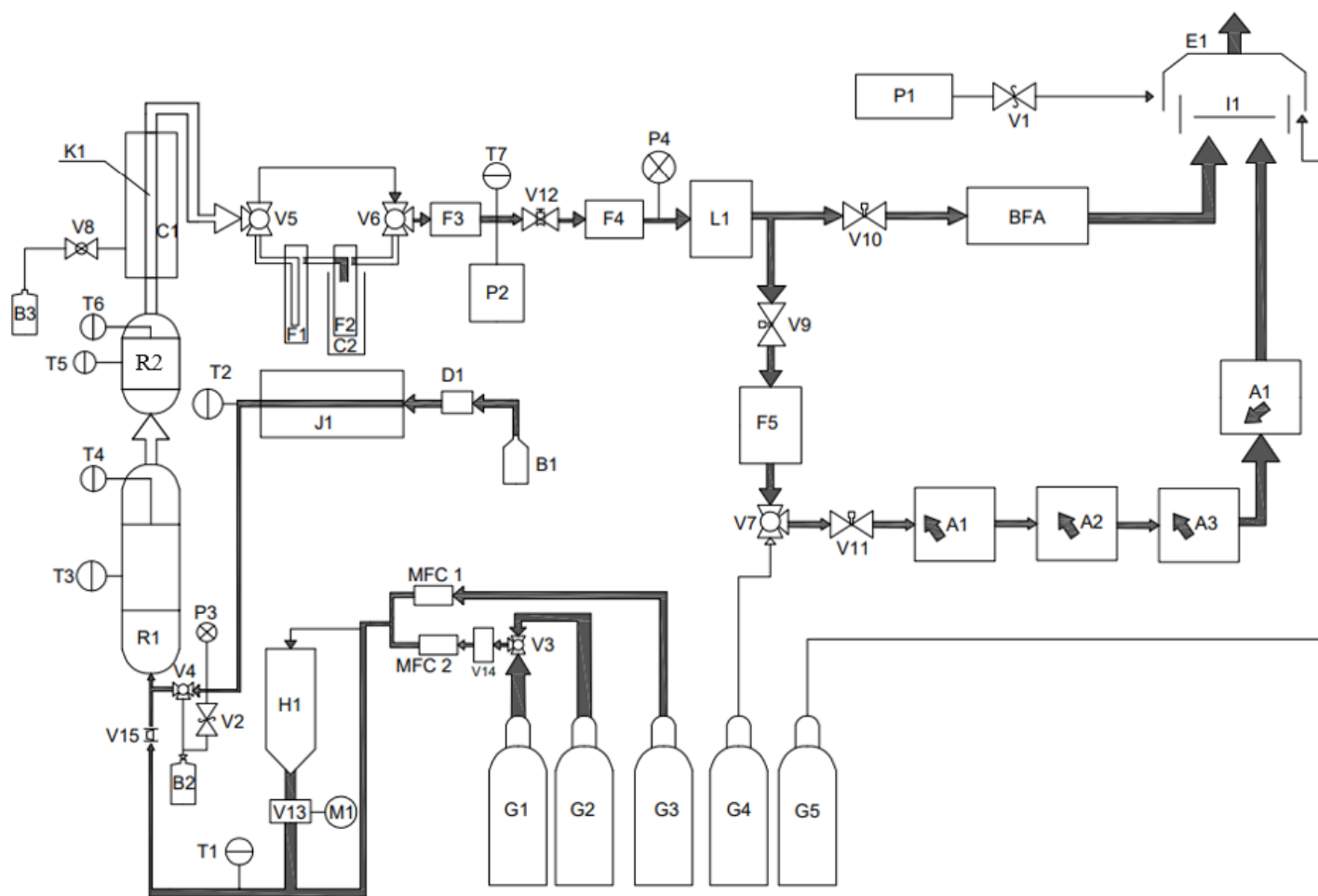


Figure 3.2 Flow sheet of experiment process

- A1: H₂ analyser
- A2: CH₄ analyser
- A3: CO analyser
- A4: Multiple analyser
- B1: DI water
- B2,3: Drain
- BFA: Back flow arrestor
- C1: Cooler (ice or dry ice)
- C2: Cooler (ice)
- D1: HPLC pump
- E1: Vent
- F1: Bubbler
- F2: Condenser
- F3,4: Filter
- F5: Moisture trap
- G1: H₂ cylinder
- G2: CH₄ cylinder
- G3: N₂ cylinder
- G4: Calibration gas cylinder
- G5: Propane cylinder
- H1: Hopper
- I1: Incinerator
- J1: Horizontal tube furnace
- K1: Tar Trap
- L1: Gas meter
- M1: DC motor
- MFC1,2: Mass flow controller
- P1,2: Pressure transducer
- P3,4: Pressure gauge
- R1: Fluidized bed reactor
- R2: Fixed bed reactor
- T1-7: Thermo couple
- V1,2: Pressure relief valve
- V3-7: Three-way valve
- V8: Ball valve
- V9-11: Needle valve
- V12: Back pressure regulator
- V13: Rotary valve
- V14: H₂ and CH₄ safety valve
- V15: Plug valve

3.3.1 Solid Feeding

The solid feeding system in this study uses a hopper to store the feedstock, a rotary valve to ensure feed it at a constant and stable rate, a shaker to help feedstock to fluently drop from hopper, and a variable speed DC motor to control the feeding rate. To ensure this feeder can stably provide a constant flow, a minimum operation flow rate should be determined before experiments. This minimum operation flow rate mainly depends on the feedstock density.

The hopper is pressurised with the carrier gas so that it can deliver solids to a high-pressure feeding line through the rotary valve. The minimum and terminal fluidisation velocity of the bed particles by the carrier gas are determined based on calculation and test. The method is shown in Section 3.6.1.

The structure of rotary valve used in this feeding system is shown in Figure 3.3. A 3.9 mm Swagelok plug valve (SS-4P4T) was modified to make this rotary valve. A hard cotton ball put in the centre of valve passage is used to block the passage and form two back to back cups of the same size. A DC motor replaced the handle of the plug valve and is used to make the cups rotate continuously. During operation, the feedstock will drop from the hopper and fill the cup. Then the rotating valve lets the feedstock to drop into the feeding line, where it is carried by the high velocity gas flow into the fluidized bed reactor. Based on the diameter of cups on the rotary valve, the particle size of feedstock should not be larger than 300 μm , which was calculated recorded by previous research using the same experimental system.^[115] This is because feedstock with a diameter larger than 300 μm would only allow a very limited number of particles to pass the rotary valve. Moreover, the sample may get stuck in the valve if the particle size is too large.

Based on requirement to perform high-pressure experiments, the whole feeding line is made of stainless steel. The motor used in these experiments can provide a rotation speed range from 0.7 to 5.4 g min^{-1} proportional to input voltage. The calibration curve of relationship between input voltage and feedstock flow rate is given in Appendix 2. The shaker is placed at back of hopper and drove by another motor.

The structure of the cup on rotary valve also requires the feedstock to keep an approximately uniform particle shape. According to previous tests, biomass with a needle shape can stem the

rotation of the valve. On the other hand, fine powders can adhere to the rotary valve surface and eventually make the valve to get stuck when too many particles have adhered. To avoid this when using lignin powder as feedstock, lignin was mixed with sand particles. This mixture will tend to flow like sand. In order to avoid sand from feeding system change the total amount of bed material fluidized in the reactor, the size of sand used to mix with lignin is such that the gas flow rate in fluidized bed reactor makes it reach its terminal velocity and be blown out from the reactor to be collected in tar trap. In experiments with catalyst and CH₄, it was observed that lignin needs to be further pre-oxidated to prevent blockages happening in the spout line. This pretreatment consisted of mild oxidation in air atmosphere at 250 °C and 1 bar for 1 hour. Pre-oxidated lignin was mixed with sea sand in a 3:1 sand:lignin ratio for feeding to the reactor. As the sand injected with lignin would change the bed length, (according to the tests, even after sieving, part of the sea sand mixed with lignin can still stay or drop back into the fluidized bed) the initial amount of sand used as bed material in these experiments was decreased from 60 g in only CH₄ experiments to 45 g.

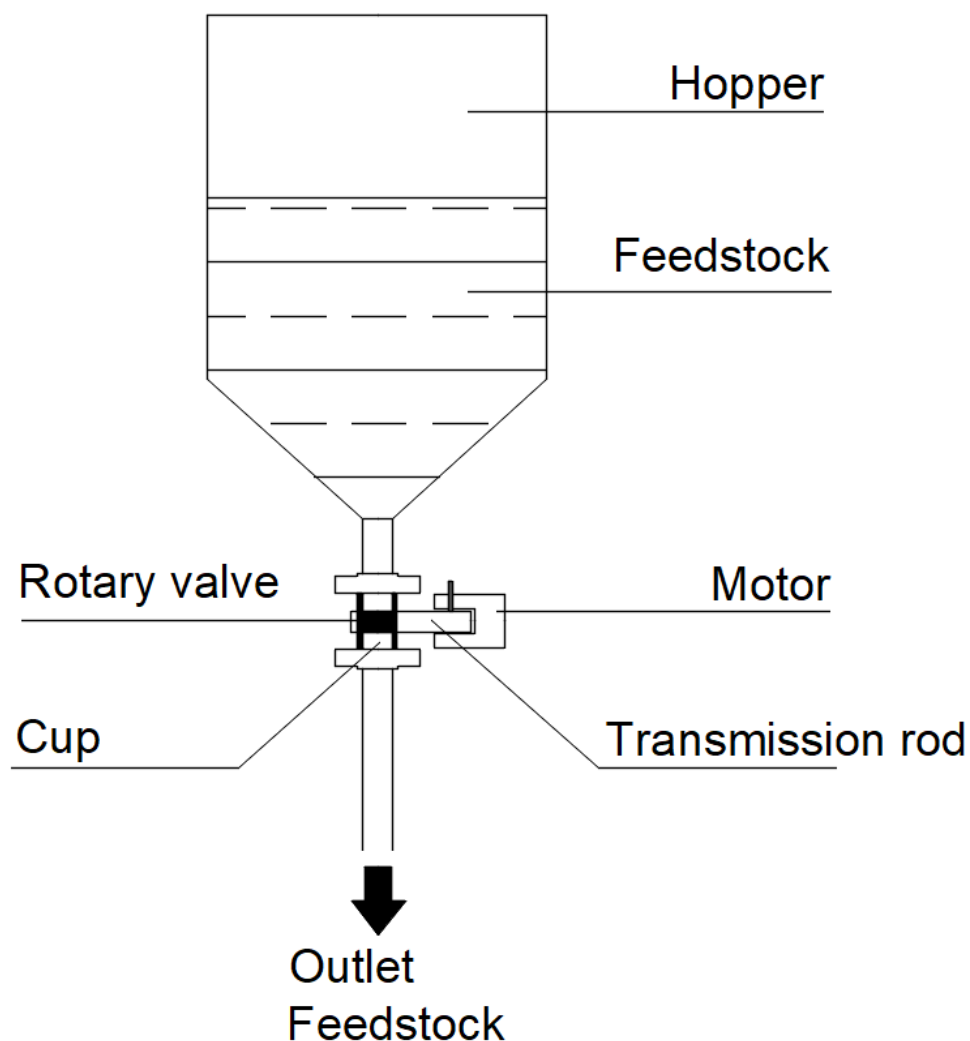


Figure 3.3 Hopper and Rotary valve

3.3.2 Gas Supply

Pure N_2 , H_2 , CH_4 gas cylinders from BOC are used to supply gas in these experiments. In experiments at pressures closed to atmospheric, all gases were operated at 2 bar_a. In high pressure experiments, all gases were provided at 10 bar_a. Two mass flow controllers were used to control the gas flow, one connected to the CH_4 and H_2 cylinders and the other to the N_2 cylinder. A bubble meter was used to calibrate the N_2 curve, as shown in Appendix 3. The H_2 and CH_4 flow rates are calculated based on a correction factor. The formula provided to calculate the correction factor (CF) given by manufacturer is:

$$CF = \frac{c_{p1}\rho_1}{c_{p2}\rho_2} \quad \text{Equation 3.1}$$

Where C_p ($\text{J g}^{-1} \text{K}^{-1}$) is the specific heat capacity and ρ (g L^{-1}) is the density. Subindex 1 refers to the calibrated gas, and 2 to gas to be measured.

3.3.3 Fluidized Bed Reactor

A $1.72 \times 0.95 \times 1.80 \text{ m}^3$ cabinet is used to place the fluidized bed reactor and protect the operator during experiments. Figure 3.4 shows the structure of fluidized bed reactor. Its main body consists of an Incoloy Alloy 800 HT tube in which an inner quartz liner is fitted. The liner is necessary as Incoloy tube contains some elements which can catalyse lignin pyrolysis and steam reforming reactions. The chemical composition of Incoloy Alloy 800 HT is shown in Table 3.2 [115]. This is a material that has good temperature and pressure resistance.

The Incoloy tube used in this fluidized bed reactor is 34 mm inside diameter, 7 mm wall thickness and 504 mm length. Wall thickness of Incoloy tube is determined by requirements of operation performance. Based on the design information of experimental system, this Incoloy tube should be replaced after it works maximum 1000 hours at 1000°C and 40 bar_a or 1050°C and 30 bar_a. The calculation of the minimum wall thickness to achieve this performance requirement is given in Appendix 1. The quartz liner placed inside the Incoloy tube is 270 mm in length with 2 mm wall thickness. As shown in the Figure 3.4, the bottom part of quartz liner is a cone shape. The inside diameter of its top circle is 28 mm and inside diameter of its bottom circle is 13 mm (see Figure 3.4). This shape allows the quartz liner to sit on a supporting ring, which is located at the end of gas and solid spout feeding line.

All gas and solids are fed into the quartz liner through the hole opened in the centre of the supporting ring. A layer of ceramic fibre wool, which is placed between bottom of quartz liner and top surface of supporting ring, and a 32 mm o.d., 12.5 mm i.d. and 20 mm height cylindrical stainless counterweight with a hole in the center are used to press the quartz liner against the spout and achieve good sealing. The bed material and fed lignin are fluidized inside the quartz liner.

Table 3.2 Chemical composition of Incoloy Alloy 800 HT

Element	Percentage, %
Ni	30-35
Cr	19-23
Fe	39.5
C	0.06-0.1
Mn	1.5
S	0.015
Si	1
Cu	0.75
Al*	0.15-0.6
Ti*	0.15-0.6

The reactor is sealed by two flanges located at both ends, which connect with other parts of system. Half-moon rings, which are fitted in the grooves on the reactor shell in both edges, are used to locate the place of inner flange. Flanges are fixed by 8 M10, 50 mm stainless steel bolts. A 48 mm o.d. 37 mm i.d. 2 mm thickness copper gasket is placed between the outer flange and end of reactor to seal the flange. The outer centres of flanges are welded with a 7.9 mm fitting and 15.9 mm straight unions respectively. Using these unions, the bottom outer flange is linked to the upstream spout line and the top outer flange is connected to the tar trap. The reactor is clamped by four half-moon shape electrodes at both top and bottom positions. These electrodes provide the Joule heating to the reactor as well as fix its location.

A back-pressure regulator (maximum 103 bar, Tescom Corporation) installed after the gas cleaning system is used to control the pressure of reactor. Two pressure sensors are separately placed in the gas feeding line and just upstream of the back-pressure regulator.

In fluidized reactor part, two K-type thermocouples are placed to separately detect temperature of the reaction area inside the quartz liner and at the outer reactor wall surface to ensure no overheating takes place. Pressure and temperature data were logged into on-line computer and software.

Heating electrodes are powered by an industrial power source and three transformers, which

include one 200-250 V, 32 A max variable transformer and two fixed step-down transformers (with 250/ 48 and 230/10 coil ratio, respectively). This arrangement enables operation of the electrodes at 1.7-2 V and maximum 8 kW power output. All electrodes are fixed on parallel copper bars that link with the transformers. The two copper bars on the top of reactor are fixed to the cabinet as illustrated above, while the copper bars at the bottom of reactor are mobile and connected by 32 insulated copper cables. The cables are covered by maximum 250 ° C heat resistant plastic. To meet the demand of experiments set point higher than 250 ° C, 3.2 mm copper tube wraps around the copper bar between cables and reactor, allowing cooling water to continuously flow during experiments.

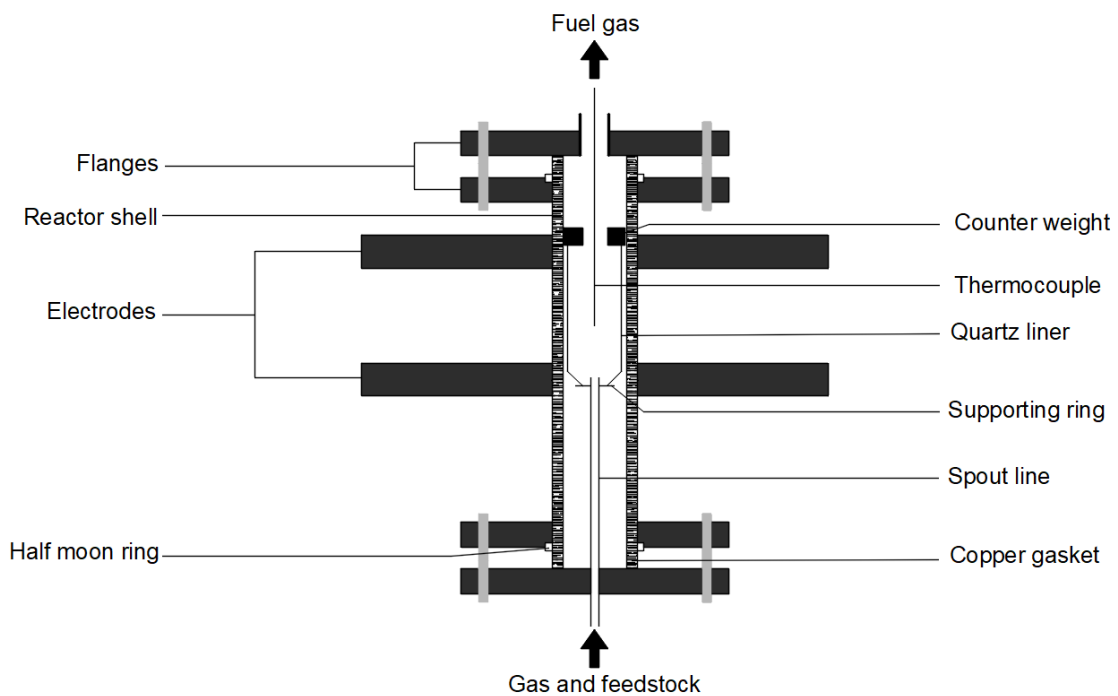


Figure 3.4 Fluidized bed reactor

3.3.4 Fixed Bed Reactor

In experiments with an ex-situ catalyst, i.e. a catalyst placed downstream from the pyrolysis reactor, a catalytic fixed bed reactor was placed downstream from the fluidized bed reactor in a two-stage reactor configuration.

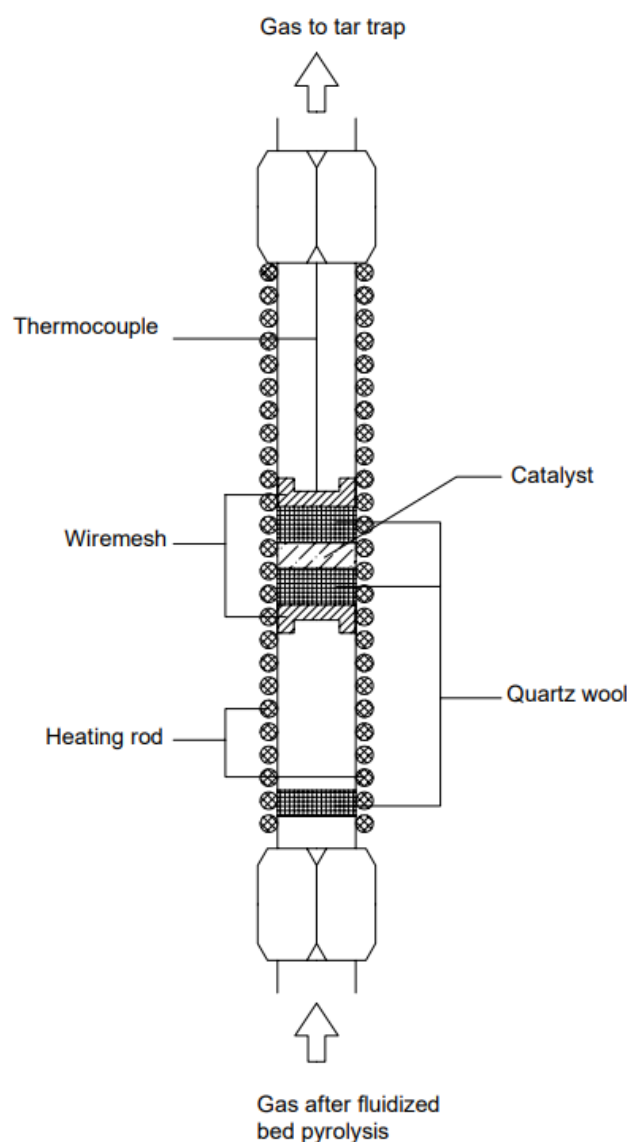


Figure 3.5 Fixed bed reactor

This fixed bed reactor consists of a 295 mm long stainless steel tube (15.9 mm o.d. and 1.2 mm wall thickness). To ensure the operating temperature was stable, the catalyst was placed at the midpoint of whole tube. Two layers of quartz wool, which can withstand up to 1050 ° C (Azpack), were used to hold the catalyst in place, preventing it from being carried away by the gas flow. Two other stainless steel wire mesh pieces were used to fix the position of catalyst and quartz wool. The bed temperature was measured by a K-type thermocouple, directly above the top of the catalyst bed, as shown in Figure 3.5.

As in experiments simultaneously involving lignin some solid can flow out from the fluidized bed reactor, another quartz wool plug was inserted at the inlet of this reactor to prevent these

solids from reaching the fixed bed reactor and affecting the results. A Briskheat Z764507 heating tape ($W \times L = 1 \text{ inch} \times 8 \text{ ft}$, 240 V AC, working up to 760°C , 0.02 W mm^{-2}) controlled by a temperature feedback controller with an output voltage of 50 V. A K-type thermocouple was placed on the outer surface of the tube to provide the feedback signal for controller. This heating tape was broken after fewer than 10 experiments. Layers of Superwool were wrapped around the heating tape for insulation.

3.3.5 Steam Generator

The steam generator used in this system consisted of an HPLC pump (CM4000 multiple solvent delivery system, LDC/Milton Roy), a horizontal tube furnace (1 kW, Carbolite Furnaces) and trace heating lines. Steam was only used in a blank experiment to test the difference on H_2 generation ability from CH_4 in DMA reaction and CH_4 steam reforming reaction. This steam generator is illustrated here to ensure the integrity of whole system.

As shown in Figure 3.6, water was pumped through a 12.7 mm i.d. and 0.89 mm wall thickness fixed stainless steel tube that ran inside a furnace, which is connected from one end to the HPLC pump (through another 1.6 mm stainless steel tube) and from the other end to a three-way valve (through a 6.4 mm stainless steel tube). To avoid dangerous over-pressurisation in case of blockage, the system is connected to a pressure relief valve (Figure 3.6). The other two ends of the three-way valve are linked with the fluidized bed reactor and a drain that feeds a transparent glass bottle. This configuration is set to make sure H_2O flows into the fluidized bed as steam. During the experiments, the three-way valve is first switched to the drain side and water flows into the transparent glass bottle. After the tube can continuously supply steam, the position three-way valve is changed to send the flow to the fluidized bed reactor.

Between the three-way valve and the bottom of fluidized bed reactor, steam mixes with solid feed in a vertical tube. The solid feed in this study is mainly lignin. Both of them tend to absorb water strongly, and this leads to tube blockages and poor flowability. This can be mitigated by heating the steam lines between the furnace and fluidized bed reactor and tubes between fluidized bed reactor and the bottom of solid feeding system. Heating tapes (310 W, 120 V, working up to 480°C , FGS051-060, Omega Engineering) were used for this purpose.

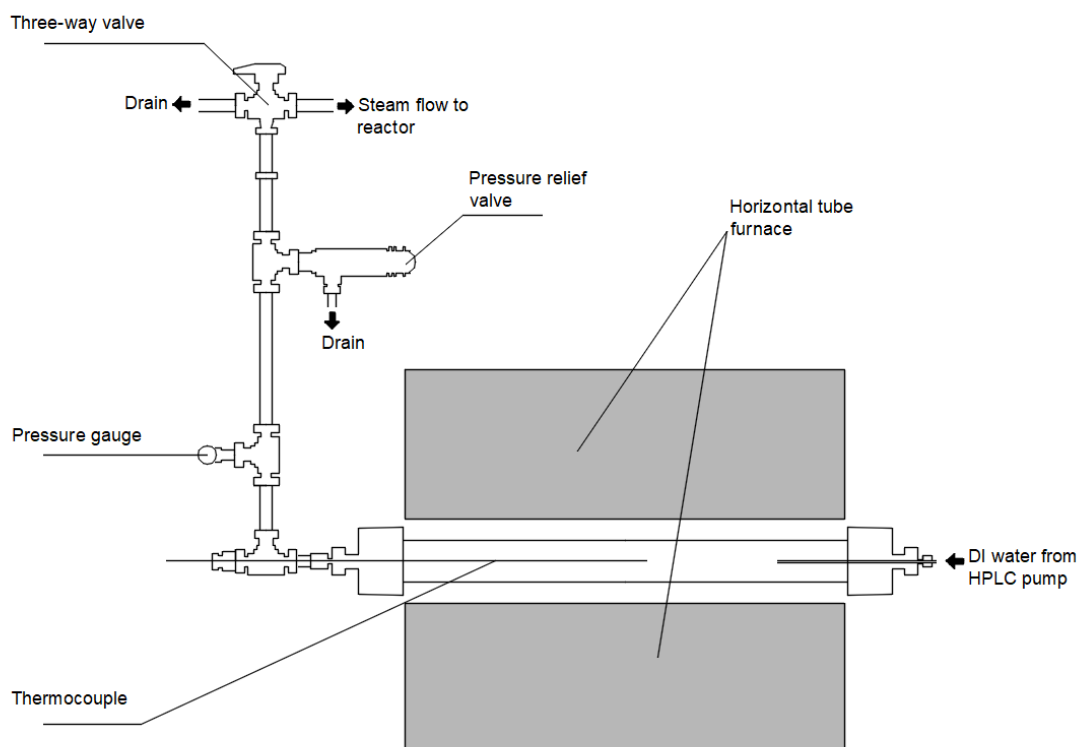


Figure 3.6 Steam generator

3.3.6 Tar Trap and Exhaust Gas Treatment

The tar trap used in these experiments consisted of a 15.9 mm stainless steel tube inside a large top open stainless steel cylindrical container (Figure 3.7). During experiments, the cylindrical container was filled by ice or dry ice to cool the gas exhaust from reactor which flows in the inner tube. The water generated from ice melting drains into a bottle linked with a Swagelok plug valve and a 6.35 mm stainless steel tube connected at the bottom of the cylindrical container. To improve the surface area of tar trap tube and collect oil products, a $200 \times 500 \text{ mm}^2$ wire mesh sheet is be rolled into a roll and placed inside the tube. Due to the special design of feeding system used in this study, the wire mesh sheet must also play a role in collecting the sand entrained in the outlet gas from the fluidized bed reactor. A glass wool ball (extra fine, Assistant) is placed at the end of the tar trap to ensure that no sand enters the downstream gas line leading to the analytical equipment. Temperature inside the fluidized bed reactor is read by a thermocouple inserted from the top of tar trap and directly placed at the middle of the fluidizing bed zone.

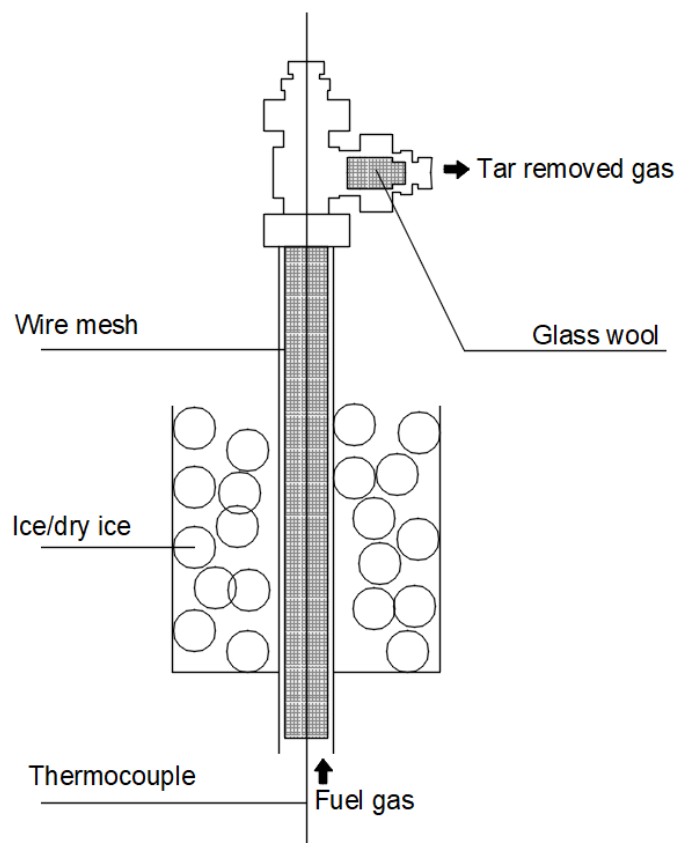


Figure 3.7 Tar trap

The outlet of the tar trap is connected with a gas cleaning system. This system consists of a bubbler, a condenser, and filters, all connected by a gas line. Both bubbler and condenser are made of stainless steel and can operate under elevated pressure. The gas leaving the tar trap first passes through the liquid contained in the bubbler before reaching the outlet. According to solubility analysis, DI water is chosen as the liquid in the bubbler to remove NH_3 and H_2S , which are the main harmful gases generated from lignin or biomass pyrolysis. To ensure the end of inlet gas tube is fully immersed under DI water, 5 mL DI water is loaded in the bubbler before each experiment. As the online gas analysers might be harmed by steam, a condenser is placed after the bubbler to collect it. The stainless steel condenser itself is empty before experiments. A plastic volumetric cylinder containing an ice-water mixture is placed around the condenser to cool it. The whole condenser is fully immersed into the ice-water bath. After the condenser, a high pressure filter (0.3 μm element pore size, GE-15K-FC-03, Swagelok) is placed to remove any potential light oils not fully recovered in the tar trap and condenser, and

prevent this light oil from damaging the back pressure regulator and gas analysers. Additionally, an atmospheric pressure filter (Balston filter element 100-12-BQ, Parker Hannifin Ltd.) is placed downstream from the back pressure regulator. (bubbler and condenser detail is shown in Figure 3.8 and the placement of filters and pressure regulator was shown in Figure 3.2)

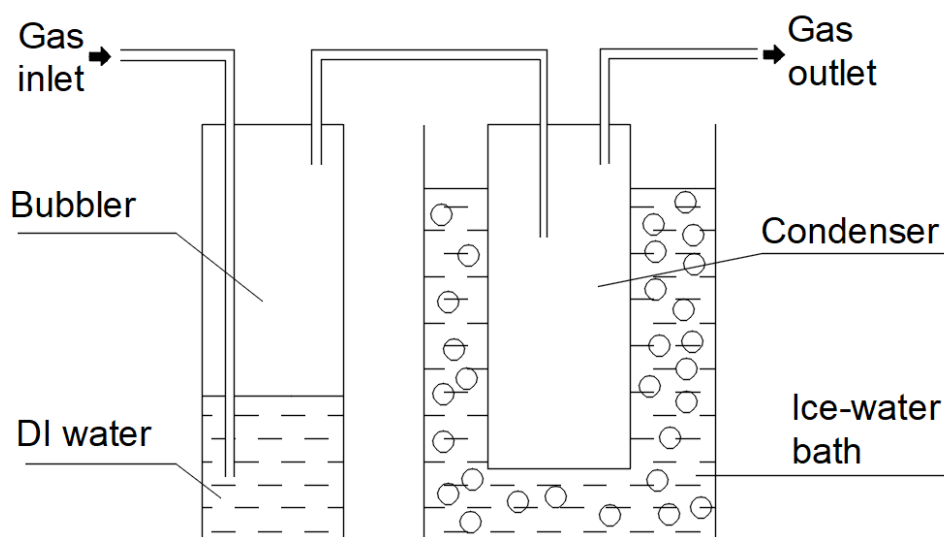


Figure 3.8 Bubbler and condenser

3.3.7 Online Gas Measurements

Online gas analysers in this experimental system mainly measure four gases: CO, CO₂, H₂ and CH₄. Four IR online gas analysers are used, one for each of CO, H₂ and CH₄ in addition to a CO plus CO₂ multi-gas analyser. After clean gas passes through the gas meter (Model G4, Metrix Grupa Apator), the stream is separated into two flows. One of them flows directly to the burner to eliminate any toxic and flammable gases. Another flow is first further dried by passing it over a transparent quartz tube containing silica gel. The dried gas flows into the online gas analysers through a stainless steel gas line. In the middle of this gas line, a Swagelok plug valve is installed to enable the operator to collect gas for GC-TCD analysis in gas bags.

3.3.8 Gas Burner

As the exhaust contains flammable gases like H_2 , CH_4 and CO , a burner is set before the product gas is discharged into the ambient. Propane (Size-B, 34-B, BOC Ltd.) is used as gas feed to the burner. To ensure no backflow happened, a backflow arrestor (RF53N, Witt Gas Techniques Ltd) is installed at the end of gas line.

3.4 Experimental Procedures

This section illustrates the detailed procedures followed for catalyst reduction and pyrolysis experiments. All experiments are based on the system described above. The catalyst reduction experiments were done separately for catalyst analysis as well as combined with pyrolysis experiments. The experimental procedure can generally be divided into five steps: system assembly, leak test, heating up, reaction and shut down.

3.4.1 CH_4 Pyrolysis without Solid Feedstock

3.4.1.1 Catalyst Reduction Experiments

Catalytic activity tends to be greater for metals in elemental or reduced oxidation states rather than their oxides. To compare this difference and obtain a catalyst with more catalytic activity, the as-received metal oxide catalysts need to be reduced. Catalyst reduction experiments were carried out in a H_2/N_2 mixture as feeding gas in the absence of solid feeding. That means solid feeding does not need to be operated and does not need to be disassembled if it has been cleaned and well connected before.

The bottom flange of reactor part was always kept assembled and sealed with the copper gasket as illustrated in Section 3.3.3. This bottom flange was only disassembled for cleaning by removing an oxide layer from the electrodes. Before assembling, a vacuum cleaner was used to clean the inner surface of the Incoloy tube and the top ring surface of the spout line to avoid bed material or catalyst left from the previous experiment to jam the quartz liner. After cleaning, the state of kaowool blanket placed at the top surface of spout line, which is used for sealing between quartz liner and spout line, was checked. If it had obvious abrasion, it was replaced

by a new one. Then, the quartz liner was sat on the kaowool blanket in such a way its outer surface would not touch the inner surface of the Incoloy tube that acts as reactor shell. The counterweight on top of the quartz liner and top flange was placed using a copper gasket as sealer. First stage leak detection was performed when the top flange was closed. For this, a ball valve installed at the top of flange and kept closed. The mass flow controller was set for N₂ flow at 2 L min⁻¹. This first leak testing focused on the feeding system and reactor sections. After it was finished, the mass flow controller was set for N₂ flow at 0 L min⁻¹. The valve was opened slightly and the N₂ gas in the system was allowed to slowly discharge to the atmosphere. When the reading on pressure meter returned to 0, the ball valve installed on the top flange of reactor was disassembled. The mass flow controller was reset to N₂ flow at 2 L min⁻¹. The amount of catalyst to be reduced was mixed with 60 g sifted sand (Merck Chemicals Ltd, sea sand purified by acid and calcined), and the mixture was added into quartz liner from the hole on the top flange. Conditions in the quartz liner were checked after bed material and catalyst were added to ensure that they had been fluidized and no blockages took place. To avoid entrained bed material entering the gas cleaning section, a glass wool ball was placed at the outlet of the tar trap. The tar trap was then installed on the top of flange. Several superwool layers were used to wrap the reactor and flange to reduce heat losses during the experiment. The tar trap was connected to the bubbler. Bubbler, condenser, high pressure filter, back regulator, atmosphere pressure filter, gas meter, online gas analysers and incinerator were sequentially connected. In catalyst reduction experiments, bubbler and condenser did not need any special processing.

When the assembling process was completed, a second leak test for the system and outlet gas line was begun. The back pressure regulator was set to 5 bar_a under a N₂ atmosphere. Soap leak detector was used to check every fitting and connection. After all connections were found be free from leaks, the back pressure regulator was used to depressurise the system slowly down to atmospheric pressure.

When pressure was back to atmospheric, the cooling water used to protect the electrodes was switched on. Then, the main power and the transformers, which provide the heating system, were kept at standby, waiting for controlling instruction from Lab View software. An existing module programme displayed the curve of real-time temperature and gas concentration read by

the thermocouples and gas analysers, and controlled the heating rate by controlling the voltage delivered to the electrodes. This programme could use wall or reactor temperature as control target. The reduction temperature was set at 500 ° C or 550 ° C for all catalyst. Normally wall temperature is higher than reactor temperature by around 30 ° C, and it was used as control target to avoid electrodes to be overheated. The set point of the wall temperature was 50 ° C higher than designed experimental temperature. This set temperature difference is used for PID control range, which may cause the wall temperature changed in a 10 ° C range. Slightly higher set point can also avoid the effect of heat lose during gas switch.

After the reactor temperature stabilised at the designed experimental temperature, the propane cylinder that feeds the burner was opened, and the burner was ignited. When the flame stabilised, the H₂ cylinder was opened and the mass flow controllers were set to keep inlet gas as 40% H₂ and the desired flow rate which depends on different catalysts. The experiment ran for one hour to ensure reduction took place. This one hour reduction may not enough to reduce the catalyst completely, the reduction condition of catalyst will be confirmed by other analysis method (XRD) after reduction experiment. During experiment, a clean transparent glass bottle with rick was picked as container to collect catalyst. This container was filled with N₂ and sealed before use to avoid reduced catalyst to be re-oxidized during storage.

The run was finished after one hour of H₂ supply. At that point, the H₂ cylinder was closed first and the H₂ channel on mass flow controller was kept at the set value to allow residual H₂ in the regulator and gas line to flow through the system and reach the burner. The flow of H₂ sharply decreased and reached zero. When this happened, the N₂ channel on the mass flow controller was set to 2 L min⁻¹. The H₂ curve shown on programme was read as the current still exist in reactor system. When the H₂ concentration dropped to the baseline before, the propane cylinder was closed and the burner turned off. The system was then allowed to cool down and transformers and main power were switched off. Cooling water was kept running until the reactor temperature was lower than 100 ° C. When the reactor temperature reached 50 ° C, the cooling down process was considered completed, N₂ supply was shut off and the valve under the bottom flange of reactor was closed to prevent bed material and catalyst from dropping into the gas line. Then, the system was disassembled. The mixture of bed material and catalyst was stored in the N₂-filled container for further analysis.

3.4.1.2 CH₄ Pyrolysis at Atmospheric Pressure

The rig assembly process in CH₄ pyrolysis atmospheric pressure experiments was similar to the catalyst reduction experiments. Catalytic CH₄ pyrolysis experiments directly followed after the catalyst reduction process. The main difference between these two rig assembly processes was that oil generated in CH₄ pyrolysis experiments needs to be collected. This requires that before the tar trap was installed on top of the reactor, a piece of 200 × 500 mm² wire mesh should be rolled and placed inside the tar trap.

After reduction of catalyst was finished, the temperature set point was changed to 30 ° C higher than CH₄ pyrolysis desired temperature, which is usually higher than catalyst reduction temperature. During this second stage heating process, the outer cylindrical container of the tar trap was filled with ice for oil condensation and checked and refilled regularly during the experiments.

At the end of each experiment, the propane cylinder and burner were kept running until both signal curves of CH₄ and H₂ (generated by reactions) dropped back to the baseline. Oil was collected for further analysis after cooling down was finished.

3.4.2 Lignin Feeding System Test to Avoid Agglomeration

The system assembly process in tests designed to avoid agglomeration when feeding lignin were the same as the CH₄-only experiments under atmospheric pressure. Before the experiment, the N₂ and CH₄ cylinder regulator outlet pressures were set at 2 bar. The feeder rotary valve was disassembled for cleaning and its three O-rings were replaced before every experiment. The DC motor was connected back with the reassembled cleaned rotary valve. Kraft lignin and sand with total weight of 60 g were placed in the feeding hopper. Then, the reconnection of hopper with gas supply and the bottom of fluidized bed was completed.

During these tests, the catalyst reduction was the first step (if this test has catalyst, which is illustrated in Chapter 5), and then the temperature was increased to that of the test. The H₂ feed was changed to CH₄. When the signal of the online gas analyser reached a stable level, the DC motor used to control the rotary valve in the feeding system was switched on. After the solid feed started, a regular sound of sand hitting the surface of the spout line was heard. Absence of

this sound means the lignin and sand did not pass the rotary valve and therefore did not enter the spout line. In that case, the shaker was started to assist the sand and lignin mixture to drop through the rotary valve. After the solid mixture was successfully fed into the spout, agglomeration and blockage might begin to happen. The moment at which the sound of sand hitting on the spout line inner surface was heard was set as time zero. Each time in which the pressure provided by gauge P3 (Figure 3.2) increased by 0.1 bar was recorded. When the reading number of P3 reached 1.7 bar, the system was considered as fully blocked (the reason why 1.7 bar was specifically considered as blockage condition are discussed in Chapter 5). When P3 reached 1.7 bar, the motor used to control the rotary valve was switched off immediately. If the feed gas flow rate was reduced, the regulator outlet pressure of N₂ was slightly increased to avoid hot bed material dropping into the spout line. After making sure the bed was still under fluidization (with the gas flow rate staying at suitable levels), the mass flow controller acting on the CH₄ feeding was first closed, and the power of heating system was then switched off. The pressure in reactor was then reduced to near atmospheric during cool-down process, allowing the safe disassembling of the whole system.

The oil was collected in the same way as in CH₄-only experiments. As some of these tests only had very short operation time, no product gases were collected for GC-TCD analysis. The sand and lignin mixture left in feeding hopper was collected when disassemble the hopper and the rotary valve.

3.4.3 Kraft Lignin Pre-treatment

Two pre-treatment methods were used in this study: torrefaction and pre-oxidation. The lignin was placed in an ex-situ fixed bed reactor which had a similar arrangement to the fixed bed reactor shown in Figure 3.4. Lignin replaced the position of the catalyst shown in Figure 3.4. The torrefaction was done in pure N₂ and pre-oxidation in air atmosphere. Both of these pre-treatments had a 30 mL min⁻¹ gas flow rate, and the temperature was increased from room temperature to 250 ° C for 10 ° C min⁻¹. It was subsequently held at 250 ° C for 1 hour.

3.4.4 Lignin Pyrolysis in CH₄ Atmosphere

The lignin and CH₄ simultaneous pyrolysis experiment was on CH₄-only experiment. In atmospheric pressure experiments, the rig assembly process was the same as for the catalyst reduction experiment. After catalyst reduction, the gas flow into the reactor was changed from H₂-N₂ to CH₄-N₂ mixture for 5 min to make sure the fluidized bed atmosphere reached a stable point and the online gas analyser was able to detect and measure CH₄. At the same time, the temperature of the reactor was raised to the experimental set point. The feeding operation was the same as illustrated in Section 3.5.2 with the solid mixture replaced by pre-oxidated lignin and sand. The product collection process was also the same as in CH₄-only experiments.

In this study, two high-pressure experiments were done. The leak test of these experiments was different to atmospheric pressure experiments, being completed at 5 bar above the designed experimental operating pressure. The temperature difference between wall temperature and set temperature can be larger under high pressure experiments than under normal pressure experiments. This was due to the gas flow rate of N₂ and CH₄ needed to keep fluidization being higher in high pressure experiments, and therefore requiring more energy to reach the set temperature. The gas flow rate and the system pressure were changed in steps up to the set point during heating up to ensure appropriate bed fluidization. After each experiment, the system was also depressurized in steps and the inlet gas flow was slowly decreased to 2 L min⁻¹ to avoid too much char from entering the tar trap.

3.4.5 In-situ and Ex-situ Catalyst Experiments

The in-situ and ex-situ catalyst experiments had a similar procedure with lignin and CH₄ simultaneous pyrolysis experiments. The difference is illustrated below. Firstly, two layers of wire mesh and quartz wool illustrated in Section 3.4.2 were weighted and placed halfway up the fixed bed reactor, and 2.5 g or 5 g of the ex-situ catalyst was placed between them (as shown in Figure 3.4). During the rig assembling, the prepared fixed bed reactor was installed between the fluidized bed reactor and the tar trap. A thermocouple placed inside of fixed bed and touched with the bed to measure the bed temperature, and another thermocouple was placed at the half of fixed bed outer wall which was used as the feedback signal to control the reactor temperature.

Then, heating tape was wrapped around the reactor and layers of insulating superwool was used to cover the heating tape and the reactor tightly. The procedure during and after experiments was the same as in lignin and CH₄ simultaneous pyrolysis experiments with in-situ catalyst only.

3.5 Analytical Methods

In this part, different methods used to analyse gas generated from the reaction, oil collected from the tar trap, catalysts made or received and solid feedstock (lignin and biomass) are described. A dry gas meter was used to measure the volumetric flow rate, and several online gas analysers and GC-TCD were used to determine the gas concentration. The components contained in oil and their concentrations were tested by GC-MS and gas chromatography with flame ionization detector (GC-FID). X-ray diffraction (XRD) and X-ray fluorescence (XRF) were used to analyse the elemental and material composition in the catalysts. Scanning electron microscopy (SEM) was used to observe the surface and determine the level of carbon deposition state as well as other properties of the catalysts. Thermochemical properties of lignin and biomass were tested by thermogravimetric analysis (TGA).

3.5.1 Gas Analysis

3.5.1.1 Dry Gas Meter

The function of dry gas meter (Model G4, Metrix Grupa Apator) used in this study was to monitor the total volumetric flow rate of gas product from the reactor. Different known volumetric flow rates of N₂, which can be obtained from the calibrated mass flow controller, were used to pass this dry gas meter as data point of calibration. The calibration results are shown in Appendix 4. During experiments, the reading data on dry gas meter was recorded every 2 mins. The volumetric flow rate of gas flows (F_{out}) in the reactor can be calculated based on two readings as:

$$F_{out} = \frac{\Delta V}{\Delta t} \quad \text{Equation 3.2}$$

where Δt (min) is the time interval, and ΔV (L) is the corresponding gas volume difference.

3.5.1.2 Online Gas Analysers

Online gas analysers are used to monitor the concentration changing curve of four main fuel gases that existed in reactor. They were tested separately by a Hitech K1500 H₂ analyser, a CH₄ analyser from ADC, a CO analyser from ADC and a multi-gas analyser (Servomex Xentra 4200) for CO and CO₂. The measuring rages of these online gas analysers are shown in Table 3.3.

Table 3.3 Measuring rages of online gas analysers

	Range
CO ¹	0-60%
CH ₄	0-20%
CO ²	0-25%
CO ₂	0-100%
H ₂	0-100%

¹ ADC, ² Servomex Xentra 4200 multi-gas meter

In previous work^[115] using this experimental system, online gas analysers were directly used to record concentration of the gases. The reasons why they were not used as an accurate reading of concentration are: (1) the H₂ concentration cannot be observed in real-time, cross calibration should always be done after every experiment; (2) cross calibration becomes very difficult when several gases are present, especially when organic gases which cannot be detected by online gas analysers are generated in reactor, the result of cross calibration would have a large error; (3) CH₄ concentration is unknown because it is much larger than the range of CH₄ analyser (0% to 20%). However, online gas analysis has the advantage that it can be used to observe the changes in gas concentration trends, which cannot be observed on GC-TCD. This advantage was used to monitor the gases, specially at sharp changing points, and check if the stable state had been reached.

3.5.1.3 GC-TCD

GC with thermal conductivity detector was used to test the concentration of each gas exist in sample gas collected directly from experimental system at certain time intervals. Gas bags, which had been evacuated, were used to collect gas at 1, 10, 20 and 30 minutes after CH₄ was introduced in the reactor in every pyrolysis experiment. In GC-TCD analysis, a 250 μ m syringe was used for injection. Before injection, it was cleaned 3 times using sample gas in the gas bag. Then, 100 μ m of sample gas were drew out from the gas bag and injected in the GC-TCD.

The temperature programme applied consisted of holding at 30 °C for 5.5 min, and then increasing to 90 °C at 20 °C min⁻¹. Temperature was held at 90 °C for 2.5 min and then ramped to 100 °C at 20 °C min⁻¹, temperature at which it was held for 3.5 min. The detector temperature was 150 °C.

The peak area and elution time of each peak were recorded separately. The peak area was used to calculate the concentration of the gas and peak elution time was used for identification against a standard gas mixture.

A calibration gas (1% n-butane, 1% propylene, 20% CO₂, 10% CH₄, 1% propane, 1% ethane, 20% CO, 20% H₂ balance in He) was used to do the GC-TCD calibration. The response factor (RF) of each gas obtained from calibration is shown in Table 3.4.

Table 3.4 Response factors on GC-TCD

Proof standard gas	Response factor
H ₂	5.07×10^{-4}
N ₂	7.03×10^{-6}
CO	7.01×10^{-6}
CH ₄	1.12×10^{-5}
CO ₂	7.01×10^{-6}

The formula used to calculate the concentration of certain gas is:

$$C_{gas1} = RF_{gas1} \times A_{gas1} \quad \text{Equation 3.3}$$

Where $C_{\text{gas}1}$ is the concentration of single gas 1, and $A_{\text{gas}1}$ is the peak area of single gas 1 obtained from GC-TCD.

3.5.2 Oil Analysis

3.5.2.1 Oil Measurement

The oil generated in pyrolysis experiments was washed with a measured volume of chloroform as solvent. Then, the oil + solvent solution was passed through a vacuum filter for 3 times to remove the solid particles. This filtered solution was evaporated on a rotary evaporator with rotation rate set as 55 rounds min^{-1} and oil bath temperature 70°C at atmospheric pressure. When the solution was reduced to around 4 to 10 mL, the remaining volume was collected and measured for GC testing. This is because some light organic compounds, for example benzene, evaporate under 70°C . If all solvent were removed, a significant fraction of light organic compounds would be lost.

3.5.2.2 GC-FID

GC with flame ionization detector was used to measure the benzene concentration in the oil generated from CH_4 pyrolysis. GC-FID is more sensitive to low concentration compounds in solution when compared with GC-MS (Gas chromatography- mass spectrometry). The amount of benzene generated directly from benzene DMA reaction is not large. GC-FID is a suitable method to detect it.

The filtered solution of oil + mixture solvent obtained from CH_4 pyrolysis experiments was used to do the GC-FID test. A $1\ \mu\text{m}$ syringe was used as injector. Before injection, the syringe was cleaned 3 times using as solvent a mixture of chloroform and methanol (volume ratio 4:1) and other 3 times cleaning by sample solution. This care was taken because the response of GC-FID is very sensitive and impurities remaining in the syringe would cause much noise in the chromatogram. After cleaning, $1\ \mu\text{m}$ sample solution was taken by syringe and injected.

The temperature programme applied consisted of the oven first held at 40°C for 1 min, then heated to 350°C at $15^{\circ}\text{C min}^{-1}$ and held for 2 min. Finally, the oven was heated to 380°C at

25 °C min⁻¹ and held for 10 min. Calibrations were performed to calculate the solvent and actual sample weight in all experiments.

As with GC-TCD, the peak area and peak appeared time were recorded to calculate the concentration of compounds and to determine which compounds corresponded the peak. In CH₄ pyrolysis experiments, benzene was the only compound contained in oil. A calibration based on a series of standard benzene at different concentrations was done based on the same operation method on GC-FID with methane pyrolysis.

3.5.2.3 GC-MS

The GC-MS&FID used in this study consisted of Shimadzu GCMS-QP2020 NX and Shimadzu Nexis GC-2030. This machine system can give both GC-MS and FID result for every injection. The column used in this system is SH-Rxi-5ms (350 ° C maximum temperature, 30 m length, 0.25 mm inner diameter, 0.25 µm film thickness).

In lignin and CH₄ simultaneous pyrolysis experiment, the oil product has a more complex composition. Limited by maximum temperature of column and analyser, solvent cut off time, and the low concentration of some compounds, this GC-MS can only match part of compounds peaks in oil with standard compound peaks. The compounds that cannot be detected by GC-MS or cannot be matched with standard compound were considered as the unknown compounds.

For every testing, a sample of 4.0 µL was injected into the GC-FID&MS injector in split mode and 280 ° C. The temperature programme applied in this GC system was set as first hold for 1 min at 40 ° C. And then increase the temperature to 100 ° C at a 10 ° C min⁻¹ heating rate. After hold at 100 ° C for 5 mins, the oven will increase the temperature to 320 ° C at 150 ° C min⁻¹ heating rate. Finally, the temperature will be hold at 320 ° C for 30 mins to make sure the column and detector was cleaned. The cutting off time of solvent (chloroform) was set at 5.5 min.

3.5.3 Catalysts Analysis

3.5.3.1 X-ray Diffraction

X-ray diffraction, which also known as X-ray powder diffraction or X-ray crystallography, is a rapid but non-destructive technology which can determine the positions of atoms, chemical bonds and finally assume the chemical composition of compounds in crystal by measuring the diffracted ray reflected from crystalline sample materials. The Bragg's Law (shown in Equation 3.4) is fundamental of X-ray diffraction. X-ray, which is collimated and monochromatic, generated from XRD machine will directly beam sample material. The reflected X-ray will be collected and processed to a diffraction pattern. Using this diffraction pattern to compare with the standard pattern, software X'pert can assume the crystalline form of the sample and determine the chemical composition of compounds contains in sample material.

$$n\lambda = 2d\sin\theta \quad \text{Equation 3.4}$$

Where n is positive integer, d (nm) is interplane distance, λ (nm) is wavelength of incident ray and θ is the scattering angle.

XRD technology was used to measure the catalyst as-received composition and check if the catalyst still contained metallic oxides after reduction. X'Pert from PANalytical and Xrd Highscores were used in this analysis. The X-ray generator was set at 40KV for tension and at 40 mA for current. The scan range was from 5 to 120° and the scan step size was 0.05°.

The XRD result can also be used to determine the size of the crystal for both metal and metallic oxides. Different catalyst crystal size can significantly affect the experiment results.

3.5.3.2 X-ray Fluorescence

X-ray fluorescence is a non-destructive technology that can be used to test the elemental composition of sample material. During XRF test, high energy and short wavelength X-rays was used to hit the electrons in sample material. Electrons obtained energy from X-rays and a

transition from low energy electron orbitals to high energy electron orbitals would happen when X-rays energy was higher than ionization energy. This transition would make whole atom system become unstable, and electrons on high energy orbitals would tend to lose energy and filled the vacancy caused by transition. During the process of these electrons fall from high energy orbitals to low energy orbitals, the energy lost would be emit in radiation. All elemental electrons have their unique orbitals characteristic energy. The elemental composition can be known by compare fluorescent radiation pattern with standard pattern.

XRF technology was used to determine the elemental composition of as-received catalyst. For two catalysts which have the same catalytic element but different element concentration, XRF can sperate them apart clearly. The XRF has an important error when the target sample is heterogeneity material. The unpredictability of heterogeneity error value and its irrelevance with concentration measurement made the XRF results can be incorrect in some cases, especially when the sample is heterogenous.^[159]

A PANalytical Epsilon3^{XLE} X-ray fluorecence (XRF) spectrometer was used to determine the elemental concentration in received catalyst

3.5.3.3 Brunauer-Emmett-Teller (BET)

Textural properties such as surface area and porosity of the Ni-based catalysts were analysed through N₂ adsorption in a Micromeritics Tristar analyser. The catalyst was first reduced in a fixed bed reactor under 500 °C and 30 mL min⁻¹ H₂ for 90 min. A sample of approximately 200 mg of reduced catalyst was degassed at 200 °C under N₂ atmosphere in a Micromeritics Flow Prep 060 degasser. The degassed sample was then placed in the equipment where it was analysed through a N₂ adsorption standard test method at -196 °C. Results were processed using the Brunauer-Emmett-Teller (BET) method to determine surface area for adsorption incorporating multilayer coverage and the Barrett-Joyner-Halenda (BJH) method to calculate the pore size distribution in the catalyst from the experimental isotherms.

3.5.3.4 Scanning Electron Microscopy (SEM)

SEM is an ideal method to observe structure of the nano-scale material. Different SEM can

adopt different materials testing. For example, high-resolution field emission gun scanning electron microscope, which works on low accelerating voltage, can obtain higher resolution images for nanomaterials sensitive to high accelerating voltages.

In this study a LEO Gemini 1525 FEGSEM was used to test the shape and structure of carbon generated on the surface of catalyst. This machine in the Department of Materials at Imperial College was previously used in the research of carbon nanotube and Ni-based superalloy. Both of these two elements, C and Ni, are targets of this study. These tests were done by Dr. Ware and Dr. Ardakani in the Department of Materials.

3.5.3.5 Thermodynamic Equilibrium Modelling

Aspen 11.0 (Aspen Technology, Inc) was used to calculate product composition at thermodynamic equilibrium conditions in CH₄ experiments. Aspen 11.0 was a software allows a model to be built by the user and run the simulation for this designed model. To achieve use Aspen 11.0 to simulate composition at the thermodynamic equilibrium condition, a process flowsheet should be first defined. Then, the input chemical components information and experimental condition of reactor was entered to the software and an estimation of the potential output compounds was achieved. When all information was given to software, run the simulation to obtain the composition result.

In this study, a RGibbs reactor model was employed to determine equilibrium in CH₄ only experiments. Pressure and temperature were completely constant when whole system reached equilibrium. At this stage, the Gibbs free energy is minimum. RGibbs reactor model is based on the minimisation of Gibbs free energy, which ensures the product compositions result from this reactor model was thermodynamic equilibrium result.

3.5.4 Lignin Analysis

3.5.4.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a technique by which the weight of a sample is monitored very precisely as temperature changes under a certain gas flow. TGA can be used as

a proximate analysis technique to measure the relative amounts of moisture, volatile organics, fixed carbon and ashes. A Pyris 1 TGA from PerkinElmer was used in this study. To analyse the composition of lignin as received, the TGA temperature program for proximate analysis is as follows:

- 1) The carrier gas is set to nitrogen at 40.0 mL min⁻¹
- 2) The sample is held for 10.0 min at 50.00 °C
- 3) Heat from 50.00 °C to 110.00 °C at 50.00 °C min⁻¹
- 4) Hold for 30.0 min at 110.00 °C
- 5) Heat from 110.00 °C to 900.00 °C at 50.00 °C min⁻¹
- 6) Hold for 30.0 min at 900.00 °C
- 7) Cool from 900.00 °C to 800.00 °C at 10.00 °C min⁻¹
- 8) Hold for 10.0 min at 800.00 °C
- 9) Switch the gas to air at 40.0 mL min⁻¹
- 10) Hold for 40.0 min at 800.00 °C

The weight decreased in steps 1 to 3 was the weight of moisture. The weight lost in step 4 to 7 was the weight of volatile. Fixed carbon was burned in step 10 and remaining mass is ash.

The TGA machine was also used to test the carbon deposits on the bed material and catalyst.

This temperature programme is shown:

- 1) Switch the gas to nitrogen at 40.0 mL min⁻¹
- 1) Hold for 15.0 min at 50.00 °C
- 2) Heat from 50.00 °C to 120.00 °C at 10.00 °C min⁻¹
- 3) Hold for 10.0 min at 120.00 °C
- 4) Heat from 120.00 °C to 900.00 °C at 10.00 °C min⁻¹
- 5) Switch the Gas to Air at 40.0 mL min⁻¹
- 6) Hold for 30.0 min at 900.00 °C

Moisture was evaporated out and all weight lost during step 6 represented the carbon deposits.

3.5.4.2 X-ray Diffraction Used in Ash Analysis

Ash of lignin and biomass contain several different elements, which might have catalytic

activity during pyrolysis. To figure out the detailed composition of ash, X-ray diffraction was used to analyse ashes recovered from TGA experiments.

3.5.4.3 The Recovery of Unreacted Lignin

In lignin and CH₄ simultaneous pyrolysis, it was unavoidable that some small particle size lignin was unreacted at the short pyrolysis time in the fluidized bed. This unreacted lignin should be separated from the solid collected from the fluidized bed and tar trap to obtain an accurate values of char yield and lignin conversion.

The oil product was assumed to fully leave the fluidized bed reactor, thus the solid collected from char bed did not need a process to remove oil. During oil collection from the tar trap, the solid collected trapped there was also washed with chloroform and recovered for further treatment. The chloroform insoluble solid was then mixed with solid collected from the char bed. This mixture was washed with in acetone. The fraction that can dissolve in acetone was considered as unreacted lignin while the insoluble part consisted of coke, sand and catalyst. The detail process for determination of unreacted lignin is shown in Figure 3.9.

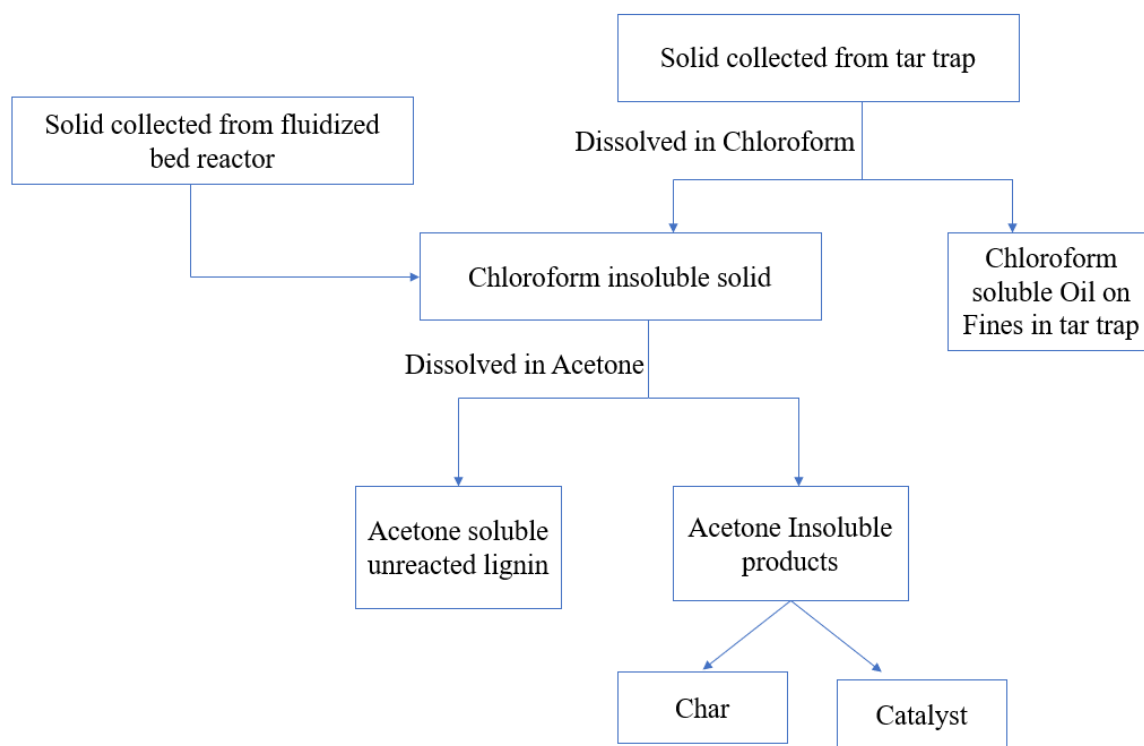


Figure 3.9 The process used to recover the solid products and unreacted lignin.

3.6 Experimental Setup Commissioning

In this section, fluidisation conditions of sand, lignin and biomass are calculated, including terminal and minimum velocity. In the second part, the calculation equation is given. Overall mass balance and steady state mass balance are illustrated in the third part. Finally, the fourth part shows experimental repeatability and discusses the error sources in the experimental process.

3.6.1 Fluidisation Conditions

In the fluidised bed experiments, the superficial velocity (U , m s^{-1}) must be higher than minimum fluidizing velocity (U_{mf} , m s^{-1}) of all solid materials in reactor. That will make sure solid materials will not drop into feed line and block the tube. The superficial velocity should be lower than the terminal velocity (u_t , m s^{-1}) of bed material and reaction feedstock (lignin and biomass) to avoid too much solid material being entrained in the flow, by-passing the reactor and being lost in the absence of a recirculating system. For the sand injected through the feeding line, the superficial velocity in the line should be higher than the terminal velocity. In this continuously fed fluidized bed reactor, the feedstock was assumed to be reacted very fast. That means in fluidized bed reactor, the reacted char will be the target used to calculate the terminal and minimum fluidized velocity.

The calculation formula of minimum fluidising velocity is shown in Equation 3.5 ^[116] below:

$$\frac{1.75}{\varepsilon_{mf}^3 \phi_s} \left(\frac{d_p U_{mf} \rho_g}{\mu} \right)^2 + \frac{150(1-\varepsilon_{mf})}{\varepsilon_{mf}^3 \phi_s^2} \left(\frac{d_p U_{mf} \rho_g}{\mu} \right) = \frac{d_p^3 \rho_g (\rho_s - \rho_g) g}{\mu^2} \quad \text{Equation 3.5}$$

where d_p is particle diameter (m), ε_{mf} is void fraction, ϕ_s is sphericity, ρ_g is gas density (kg m^{-3}), ρ_s is solid density (kg m^{-3}), μ is viscosity ($\text{kg m}^{-1} \text{s}^{-1}$), g is gravity acceleration (9.81 m s^{-2}). Gas density and viscosity data was obtained from NIST Webbook ^[117]. The data of void fraction and sphericities of sand and char can be found in D. Kunii^[116].

To separate bed material sand from the sand added in the hopper of the feeding system, the bed material sand size was chosen as 200-300 μm . Based on these particle sizes, the minimum

fluidisation velocities of sand and char under 600 °C are shown in Table 3.5.

Table 3.5 Minimum fluidising velocity (U_{mf}) and superficial velocity (U) at 600 °C

Carrier gas		Type	Particle size μm	Pressure, bar _a		
				1	5	10
U _{mf} , m s ⁻¹	N ₂	Sand	200	0.027	0.027	0.027
			300	0.044	0.044	0.044
		Char	200	0.022	0.022	0.022
			300	0.029	0.029	0.029
U, m s ⁻¹				0.185	0.133	0.084

The minimum fluidisation velocity had a negligible change with pressure between 1 and 10 bar and increased when solid size increased.

In the calculation of terminal fluidization velocity, the drag coefficient and Reynolds number were introduced. The calculation formula is shown below:

$$u_t = \left[\frac{4d_p(\rho_s - \rho_g)g}{3\rho_g C_D} \right]^{0.5} \quad \text{Equation 3.6}$$

Where C_D is the drag coefficient, which depends on Reynolds number according to the formula shown in Equation 3.7.

$$C_D = \frac{24}{Re_p} \left[1 + (8.1716e^{-4.0655\phi_s}) Re_p^{0.0964+0.5565\phi_s} \right] + \frac{73.69(e^{-5.0748\phi_s}) Re_p}{Re_p + 5.378e^{6.2122\phi_s}} \quad \text{Equation 3.7}$$

Re_p is the particle Reynolds number and can be calculated by:

$$Re_p = \frac{\rho_g u_t d_p}{\mu} \quad \text{Equation 3.8}$$

Equation 3.6 and Equation 3.8 were used to calculate C_D from Equation 3.9:

$$C_D = \frac{4d_p^3(\rho_s - \rho_g)\rho_g g}{3Re_p^2\mu^2} \quad \text{Equation 3.9}$$

Microsoft office Excel is used to adjust the data of Re_p by using Solver function to match C_D in Equations 3.7 and 3.9. Because of the complexity of these equations, it is hard to obtain the exact solution of Re_p to make C_D in Equation 3.7 equal to C_D in Equation 3.9. Thus, when using Solver function in Excel, the Re_p is changed to allow the difference between C_D values to be less than 1×10^{-4} . This Re_p was used to calculate the C_D in Equation 3.9, and the calculated drag coefficient was used in Equation 3.6 to obtain the terminal velocity. To avoid any bed material or char being blown out of the reactor, the terminal velocity of 200 μm char, which has the lowest density and particle size of all material should be higher than superficial velocity. A terminal velocity of 200 μm char at 600 °C in N_2 or steam as carrier gas is shown in Table 3.6.

Table 3.6 Terminal velocity (u_t) of 200 μm char and superficial velocity (U) at 600 °C

Carrier gas		Pressure, bar _a		
		1	5	10
$u_t, \text{m s}^{-1}$		0.55	0.43	0.37
Re_p	N_2	1.12	4.32	7.45
C_D		30.81	10.41	6.97
$U, \text{m s}^{-1}$		0.185	0.133	0.08

As mentioned above, the sand used together with lignin in the feeding system should have a particle size such that its terminal velocity is less than the operating superficial velocity. Based on the same calculations shown above, sand mixed with lignin has a particle size smaller than 150 μm .

The pressure drop in the fluidized bed reactor during operation was between 0.3 and 0.5 bar_a. A previous study based on this experimental system gave the temperature distribution of reactor.^[118] Those experiments were performed at 700 °C and with 60 g of 200-300 μm sand as bed material, which maintained fluidising bed height at 110 mm. 60 g sand provided a good and effective mixing with feedstock particles in previous research using the same reactor.^[119] In Spiegel's research^[118], this reactor had a temperature distribution that increased from 685 to

705 °C in the bottom 20 mm of quartz liner. From this position to the top of the bed, the temperature was stable and only had a 5 °C increase. Thus, the temperature distribution did not obviously affect the fluidization state in the bed.

3.6.2 Calculation in Experiments

The overall CH₄ conversion was calculated from Equation 3.10, where N is the total moles of gas and y_{CH_4} the mol fraction of CH₄.

$$X_{CH_4}(\%) = \frac{N_{in} y_{CH_4,in} - N_{out} y_{CH_4,out}}{N_{in} y_{CH_4,in}} \times 100 \quad \text{Equation 3.10}$$

The H₂ mol yield in pure CH₄ experiments was calculated from Equation 3.11 where N_{H_2} is the total mol of H₂ produced at steady state and N_{CH_4} is the total moles of CH₄ fed into reactor during steady state.

$$Y_{H_2}(\%) = \frac{2 \times N_{H_2}}{3 \times (N_{CH_4})} \times 100 \quad \text{Equation 3.11}$$

The oil, gas and solid weight yields were calculated from Equation 3.12, where W_X is weight of fraction X (oil, gas or solid product) recovered from the run, W_{CH_4} is the total weight of CH₄ and W_L that of lignin fed during the run. Equation 3.12 was also applied to the calculation of the oil weight yield from lignin in experiments in N₂ and H₂ but without CH₄ by making $W_{CH_4} = 0$.

$$Y_X(\%) = \frac{W_X}{W_{CH_4} + W_L} \times 100 \quad \text{Equation 3.12}$$

The oil weight yield from lignin (W_{L-oil}) in experiments with CH₄ was calculated from Equation 3.13, in which W_{M-oil} is the oil weight generated from the CH₄-only experiment under otherwise equivalent conditions. The assumption made in this calculation is therefore that the introduction of lignin does not affect the DMA reaction.

$$Y_{L-oil}(\%) = \frac{W_{L-oil} - W_{M-oil}}{W_L} \times 100 \quad \text{Equation 3.13}$$

The selectivity to oil (S_{oil}) in CH₄-only experiments was calculated from Equation 3.14, in which N_{C-oil} means the moles of C in the oil, mainly composed of BTEx, while the denominator is the moles of CH₄ reacted.

$$S_{oil}(\%) = \frac{N_{C-oil}}{N_{in} \gamma_{CH_4, in} X_{CH_4}} \times 100 \quad \text{Equation 3.14}$$

The selectivity to carbon formation on the catalyst (S_C) in CH₄-only experiments was calculated from Equation 3.15, in which, S_C means the selectivity of carbon, and N_C means the moles of carbon deposited.

$$S_C(\%) = \frac{N_C}{N_{in} \gamma_{CH_4, in} X_{CH_4}} \times 100 \quad \text{Equation 3.15}$$

N_C was calculated using Equation 3.16 from the weight of solid recovered from an experiment and the TGA weight loss, in which $W_{120\text{ }^\circ\text{C}}$ and $W_{900\text{ }^\circ\text{C}}$ are the sample weights on the TGA pan recorded at 120 °C and 900 °C, respectively.

$$N_C = \frac{W_{solid}}{12} \frac{W_{120\text{ }^\circ\text{C}} - W_{900\text{ }^\circ\text{C}}}{W_{120\text{ }^\circ\text{C}}} \quad \text{Equation 3.16}$$

The lignin conversion (X_L) in CH₄ and KL simultaneous pyrolysis experiment was calculated from Equation 3.17. In which W_{URL} means the weight of unreacted lignin.

$$X_L = \frac{W_L - W_{URL}}{W_L} \quad \text{Equation 3.17}$$

A series of GC-MS+FID tests were done using a chloroform and glycerol mixture to test the response factor of chloroform (details given in Appendix 6). Based on the chloroform response

factor, the weight of residual chloroform left in the oil products after evaporation can be measured. Lignin depolymerization products still contain a heavy fraction that does not elute through the GC column. The weight of these compounds out of the GC range, $W_{unknown}$, was calculated by Equation 3.18:

$$W_{unknown} = W_{oil} - (W_{known} + W_{chloroform}) \quad \text{Equation 3.18}$$

W_{oil} is the total oil weight, W_{known} means the weight of compounds detected by GC-FID and confirmed by GC-MS (because the detector of GC-FID was more sensitive than GC-MS, some compounds detected by FID were not observed by GC-MS). Thus, only compounds that can be detected by both FID and MS are considered as known compounds). $W_{chloroform}$ means the weight of chloroform left in the oil. In Chapter 5 and Chapter 6, the GC detectable oil will be called as light oil.

The compounds out of GC range include the following: firstly, large molecules that are not volatile enough to be injected or elute through the GC; second, small molecules with an elution temperature lower than chloroform, as a cut off time is used in the GC-MS to prevent the detector from being harmed by high concentration solvent, which eliminates any peaks eluting earlier than this cut off time; third, species present in only limited concentrations that cannot be detected or cannot be matched to any compound in the GC-MS database.

3.6.3 Mass Balance

The mass balance was separately calculated for CH₄ only experiments and lignin & CH₄ simultaneous pyrolysis experiments. 580 ° C, 1 bar, 2 L min⁻¹ total gas flow rate, 30% CH₄ and 5 g Ni/Al₂O₃-SiO₂ catalyst experiment was set as the common experimental condition for both mass balance calculations. The details of the results are shown below.

3.6.3.1 Mass Balance for Only CH₄ Experiment

The overall mass balance for CH₄ only experiment was 96.5% at the conditions described above (detail mass balance information is discussed in Table 3.7). This is considered a

reasonably good value for complex experiments. The deviation from 100% can be due to the reasons illustrated below. First, errors in the calculation of gas products. The outlet product gas weight was based on the sum of the volume of each gas product multiplied by its density. The concentration of each gas product was obtained from GC-TCD, but the total outlet gas volume was hand-recorded every 20 s. However, when the reduction of catalyst process ends and the H₂ channel was switched to CH₄, the outlet gas volume and concentration changed sharply. That will introduce an error for each product gas volume calculation in this 20 s. Second, an underestimation could happen when the amount of char was recorded. Because of the structure of fluidized bed reactor, the spout line should be slightly inserted into the quartz line. After every experiment, this made the char bed drop to the bottom of quartz line and this material always included a small amount of char that stayed at a place lower than the spout line injection point and could not be collected from the spout line. Third, some light oil like benzene might escape the tar trap, bubbler, and condenser and be lost during the experiment. Some oil can also be lost during solvent evaporation as the evaporation temperature was close to the boiling point of benzene. Finally, only three main gas compounds were measured. Minor products including higher hydrocarbons as C₂H₆ and C₂H₄, were not measured.

Table 3.7 The quantity of reactants and products of CH₄ only experiment at 580 ° C, 1 bar, 30% CH₄ and 5 g Ni/Al₂O₃-SiO₂ catalyst experiment

	Constituent	Weight, g
Reactants	CH ₄	15.52
	Total	15.52
Products	Char*	1.61
	Fines in tar trap	0.63
	Oil	1.43
	Gas**	11.31
	Total	14.98
Mass balance		96.5%

* The char was calculated by weight difference between the collected char bed after experiment and sand + catalyst bed before experiment.

**The sum of H₂ and CH₄ weight.

3.6.3.2 Mass Balance for Lignin and CH₄ Simultaneous Pyrolysis Experiment

The overall mass balance for lignin and CH₄ simultaneous pyrolysis experiment was 91.3%, a poorer closure of the mass balance than in CH₄-only experiment, at 580 ° C, 1 bar, 2 L min⁻¹ total gas flow rate, 1.5 g min⁻¹, sand : lignin = 3:1, 30% CH₄ and 5 g Ni/Al₂O₃-SiO₂ catalyst experiment. The reasons behind the difference are similar to those discussed above. Loss of light oil and incomplete gas analysis are thought to play a greater role in experiments where lignin was fed. Moreover, some of the small particle size sand used to dilute the lignin can flow out from fluidized reactor and pass through the gap between counter weight and the flange. This small particle size sand can enter the area between quartz line and Incoloy Alloy 800HT tube which cannot be collected after experiments. That will also contribute to an underestimation of the char amount. The weights of reactants and products in lignin and CH₄ simultaneous pyrolysis experiment are shown in Table 3.8.

Table 3.8 The quantity of reactants and products of lignin and CH₄ simultaneous pyrolysis experiment at 580 °C, 1 bar, 2 L min⁻¹ total gas flow rate, 1.5 g min⁻¹, sand : lignin = 3:1, 30% CH₄ and 5 g Ni/Al₂O₃-SiO₂ catalyst

	Constituent	Weight, g
Reactants	CH ₄	15.52
	Lignin	15
	Total	30.52
Products	Char*	6.92
	Unreacted lignin in tar trap	2.15
	Oil	4.04
	Gas**	14.75
	Total	27.86
Mass balance		91.3%

* The char was calculated by weight difference between the collected char bed after experiment and sand + catalyst bed before experiment.

**The sum of H₂, CH₄, CO and CO₂ weight.

3.6.4 Experimental Errors and Repeatability

In this section, the error sources in this experimental system are analysed. The overall errors of the gas composition and C conversion were calculated by using error propagation method. To ensure the whole system can meet the requirement of repeatability, an experiment of CH₄ pyrolysis under 600 °C, 1 bar_a and Ni/Al₂O₃-SiO₂ as catalysts was repeated 5 times.

3.6.4.1 Equipment Errors

Temperature measurement: K-type thermocouples were used as temperature measurement in this system. They have an accuracy of $\pm 0.4\%$ when employed according to the instructions from supplier. The fluidized bed reactor was set at 600 °C for pyrolysis experiments and 500 °C for catalyst reduction. The given error of each condition is ± 3.4 °C. Because of the PID controlled programme used to operate the fluidized bed reactor, the temperature of fluidized

bed reactor fluctuated within a range of ± 5 °C around the setpoint temperature at atmosphere pressure.

Pressure transducer: a back pressure regulator was used to control the system pressure to keep it within ± 0.1 bar of the desired pressure. The given pressure transducer error was ± 0.1 bar.

Mass flow controller: The reading data has a $\pm 1\%$ difference with the true input data on mass flow controller. As it has been discussed before, the setpoint on mass flow controller is very different with the actual flow rate. To know the relationship between the set data and actual flow rate of each inlet gas, a bubble-meter was used to do the calibration. During the bubble-meter calibration, its accuracy was ± 10 mL. When counting the interval between bubbles, human reaction time was taken as 0.45 s.^[120] The formula used to calculate the calibration gas flow errors is shown in Equation 3.19, which can be used to calculate the error from the combined two factors.^[121]

$$\frac{\Delta F}{F} = \left[\left(\frac{\Delta V}{V} \right)^2 + \left(\frac{\Delta t}{t} \right)^2 \right]^{0.5} \quad \text{Equation 3.19}$$

The total error including equipment error was calculated based on Equation 3.20:

$$\Delta C = [\Delta A^2 + \Delta B^2]^{0.5} \quad \text{Equation 3.20}$$

Where $C=A+B$, and A, B are independent.

Steam generator: The error of HPLC pump has been given by the instrument manufacturer which is $\pm 1\%$ of reading.

Solid feeder: Several factors may cause error when solid feeder operation. First, the two cups in the rotary valve have slightly different volumes, which means the feeding flowrate has a small fluctuation. This difference is less than $\pm 3\%$ based on the test results. Second, the mixture in the hopper cannot be fully homogenized, especially when the shaker is operating, and this may cause a stratification of materials having different densities. Thus, in lignin pyrolysis experiments, the shaker should not be turned on. Third, the experimental pressure

may slightly increase the feeding rate.

Gas meter: Equation 3.19 was used to calculate the error of the measured volumetric gas flow.

The accuracy of the gas meter is ± 0.1 L.

Online gas analysers: The errors of online gas analysis are a combination of not only the analyser error, but also the calibration gas and normalisation of the gas composition. However, online gas analysers in this study were only used qualitatively to monitor gas composition trends and instead accurate gas composition data was obtained from GC-TCD. Therefore, the error from online gas analysers did not affect the experiment result.

GC: All GC include TCD, FID and MS have a reading error when the peak area of the compounds was obtained. This is because the GC baseline is not always stable. Repeat experiments had been done on GC-TCD, finding an error in the range of $\pm 4\%$, the same as for GC-FID&MS is $\pm 4\%$.

3.6.4.2 Experimental Repeatability

Five repeat experiments (results shows in Table 3.9) were done under the same experimental conditions (600 °C at 1 bar_a with a 2 L min⁻¹ total inlet flow rate 80% CH₄ and 5 g Ni/Al₂O₃-SiO₂ contained catalyst.) The main products of these experiments were H₂ as gas product, benzene as oil and carbon deposit as char. The detailed information of H₂ concentration in 5 repeat experiments is shown in Table 3.9. Detailed experimental products at steady state (20 min after CH₄ introduced), their mean value, standard deviation (SD) and 95% confidence intervals (CI) are given in Table 3.10.

Table 3.9 Detail information of concentration of generated H₂ in repeat experiments

Run	Concentration of generated H ₂			
	1 min after CH ₄ introduced	10 min	20 min	30 min
1	33	27.7	30.2	
2	29.5	29.7	32.2	32.6
3	31	32.5	32.3	32.9
4	28.6	29.4	33.5	33.0
5	32	31.7	33.1	32.4

Table 3.10 Repeatability of CH₄-only experiment

Run	CH ₄ conversion, mol%	H ₂ yield, mol%	Oil yield, %
1	35.8	29.7	16.9
2	35.2	29.2	16.5
3	34.5	28.0	15.9
4	36.1	30.1	17.2
5	34.7	28.2	16.1
Mean	35.3	29.0	16.5
SD¹	0.69	0.92	0.54
95% CI²	35.3 ± 0.6	29.0 ± 0.81	16.5 ± 0.47

$$^1SD = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}}$$

$$^295\%CI = \bar{x} \pm \frac{1.96SD}{\sqrt{N}}$$

Five other repeats for CH₄ and lignin simultaneous pyrolysis experiments were done in the same conditions (580 °C at 1 bar_a with a 2 L min⁻¹ total inlet flow rate 30% CH₄, 3:1 sand:lignin dilution rate, 1.5 g min⁻¹ feeding rate and 5 g Ni/Al₂O₃-SiO₂) and are shown in Table 3.11.

Table 3.11 Repeatability of the experimental procedure

Run	Oil yield, wt. %	Gas yield, wt. %	Lignin conversion, %	Outlet gas concentration, %		
				H ₂	CO	CO ₂
1	20.7	24.6	72.5	9.3	10.2	1.1
2	21.7	23.4	72.9	8.5	11.0	1.5
3	19.9	25.1	70.8	9.5	9.8	0.7
4	20.4	24.1	72.7	9.6	10.1	1.1
5	20.8	24.3	73.0	9.5	10.1	1.4
Mean	20.7	24.3	72.4	9.3	10.2	1.2
SD	0.66	0.63	0.90	0.45	0.45	0.31
95% CI	20.7 ± 0.58	24.3 ± 0.55	72.4 ± 0.79	9.3 ±	10.2 ±	1.2 ±
				0.39	0.39	0.27

Chapter 4. Fluidised Bed Methane Catalytic Conversion by Direct Methane Aromatization and Cracking

4.1 Introduction

As is shown in Chapter 2, direct methane aromatization (DMA) is a reaction to transform CH_4 to H_2 and benzene. The by-products of DMA are toluene, ethylbenzene and xylenes as well as other aromatics observed at long reaction times. CH_4 cracking, also referred in the literature as CH_4 pyrolysis can happen in parallel to the DMA reaction and is favoured by high temperature, although the optimal CH_4 cracking temperature varies widely for different catalysts. For example, Ni-based catalysts can enable CH_4 pyrolysis to take place at 500-700 °C, while Fe-based catalysts have an optimal temperature of 700-900 °C and the range for carbon-based catalysts is 800-1000 °C.^[122]

The catalyst is a major influencing factor in DMA reaction and catalyst deactivation a major challenge given the reaction involves methane at high temperature. Strategies to reduce catalyst deactivation and keep the DMA reaction occurring at high reaction rates become an important topic. Previous study of this topic by other researcher have mainly focused on HZSM-5, Ni-based and Mo-based catalysts. But, in this study, the catalyst should also be suitable for catalysing lignin pyrolysis when choosing catalyst for DMA experiments. Previous research also mentioned that the method and environment used to reduce and active the catalyst can essentially affect the crystal domain size of catalyst, especially in Ni based catalysts.^[160,161]

In this chapter, the influence of CH_4 concentration, catalyst type and amount, temperature and experiment carried out exclusively with CH_4 (no lignin) are discussed. An optimal condition for CH_4 generate H_2 were found according to the H_2 concentration at experimental steady state and the catalyst deactivation speed.

This chapter consists of four parts. This introduction is followed by a summary of the experimental conditions used in these experiments. The third part describes the experimental results and discusses the effects of different variables. Finally, summary and main conclusions are provided in a separate section.

4.2 Experimental Methods

The fluidized bed reactor system illustrated in Chapter 3 was used to operate the CH₄ only experiments. The HZSM-5 and Ni-based catalyst were chosen as the catalysts used in this chapter. According to previous literature, HZSM-5 and Ni had ideal performance on catalyzing both DMA reaction and lignin pyrolysis (which will discuss in Chapter 5). The difference of Ni and NiO was also taken into consideration to found if reduction of catalyst can affect the result. Another variable on catalyst was the catalyst amount, high (5 g) and low (1.56 g) level catalyst amount was set to study the difference. The experiment temperatures were in a range of 550 °C (which is the beginning point of DMA reaction) to 700 °C (which is the upper limit of the optimal temperature for Ni catalyst illustrated in Section 4.1). The review of all experimental conditions is shown in Table 4.1.

Table 4.1 Experimental conditions

Run	Temperature (°C)	Catalyst	CH ₄ concentration (%)
1	700	5 g, HZSM-5	30
2	700	5 g, Ni/Al ₂ O ₃ -SiO ₂	30
3	700	5 g, Ni/SiO ₂	30
4	700	5 g, NiO/SiO ₂	30
5	700	5 g, Ni/Al ₂ O ₃ -SiO ₂	80
6	700	1.56 g, Ni/Al ₂ O ₃ - SiO ₂	80
7	550	5 g, Ni/Al ₂ O ₃ -SiO ₂	80
8	580	5 g, Ni/Al ₂ O ₃ -SiO ₂	80
9	600	5 g, Ni/Al ₂ O ₃ -SiO ₂	80
10	650	5 g, Ni/Al ₂ O ₃ -SiO ₂	80
11	700	5 g, Ni/Al ₂ O ₃ -SiO ₂	80

The oil and gas products were analyzed by GC-FID and GC-TCD illustrated in Chapter 3. TGA was used to detect the deposit carbon weight generated during experiments. Calculation equations used in this Chapter have been given in Chapter 3 (Equation 3.10, 3.11, 3.12, 3.13, 3.14, 3.15, 3.16).

4.3 Results and Discussion

This section illustrated the effect of different variables on CH₄-only experiments. These variables include: catalyst kinds, catalyst amount, reduced or as received catalyst, CH₄ concentration and temperature.

4.3.1 Catalyst Characterization

As is illustrated in 4.1, Two Ni-based catalysts were chosen as the test catalysts in this chapter. Both of them had a relatively low optimal working temperature (500 to 700 °C) which was also the optimal temperature of both DMA and lignin pyrolysis temperature. Another pure HZSM-5 catalyst without metal on it was also tested to check if Al₂O₃ and SiO₂ can affect the result of DMA reaction.

The BET analysis of catalysts used in this chapter is shown in Table 4.2. The Ni/Al₂O₃-SiO₂ catalyst had the highest specific surface area, pore volume and average pore diameter. It was chosen as the potential optimal catalyst.

Table 4.2 Textural properties (specific surface area, pore volume and average pore diameter) of reduced catalysts

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Pore Size (nm)
HZSM-5	66.1	0.3	5.4
Ni/ Al_2O_3 - SiO_2	111.0	0.3	8.7
Ni/ SiO_2	95.4	0.1	3.9
Ni/ Al_2O_3 - SiO_2 after 580 °C pure CH_4 experiment	82.8	0.4	13.6
Ni/ Al_2O_3 - SiO_2 after 700 °C pure CH_4 experiment	55.6	0.26	13.6

The hysteresis loops of the catalyst used in this chapter are shown in Figure 4.1. According to Figure 4.1 (a), the hysteresis loops of HZSM-5 is H1 type. ^[123] The pore in this type of catalyst only has uniform mesopores in a limited range. The network effect stays at minimal level in H1 type hysteresis loops catalyst. The Ni/ Al_2O_3 - SiO_2 catalyst has a H3 type hysteresis loop. That means Ni/ Al_2O_3 - SiO_2 catalyst is in a plate like particles with clear layered and in non-rigid aggregates state. The catalyst has H3 type hysteresis loop also contains a pore network which consisted by not completely filled macropores. This can also be proved by the BET pore size result. The Ni/ SiO_2 catalyst contains a H4 type hysteresis loop. This type had a similar structure with H3, but the micropore in H4 type hysteresis loop catalyst was more filled.

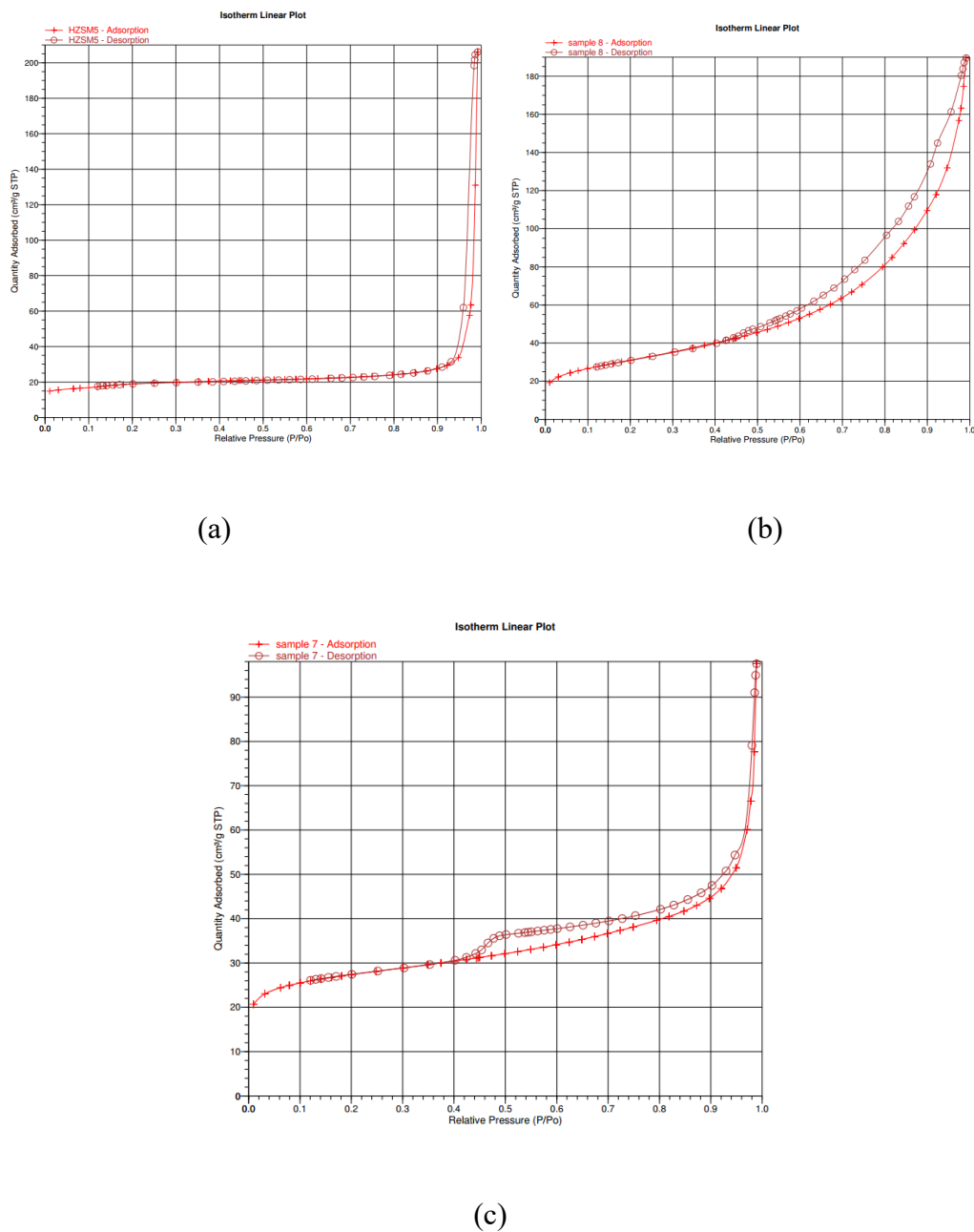
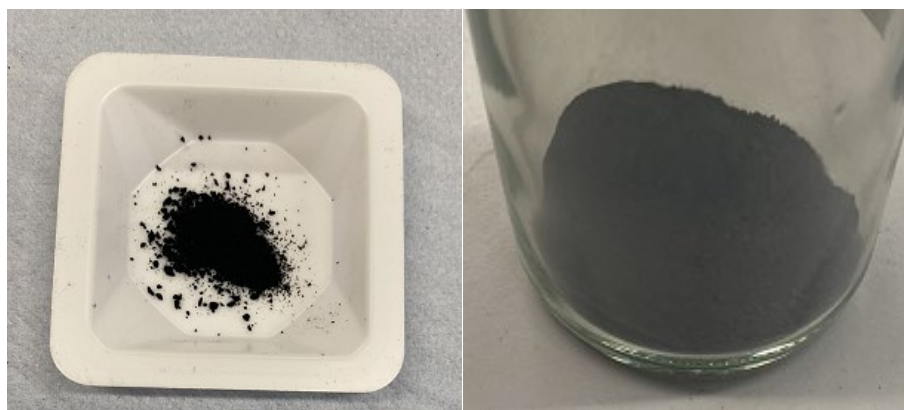


Figure 4.1 Hysteresis loops of (a) HZSM-5, (b) Ni/Al₂O₃-SiO₂, (c) Ni/SiO₂ catalyst

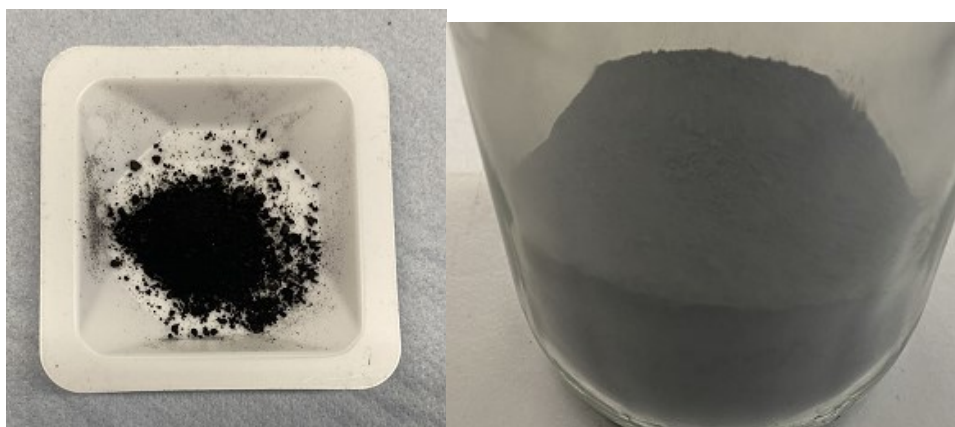
The visually morphology of these three catalysts is given in Figure 4.2. The as received Ni/Al₂O₃-SiO₂ and Ni/SiO₂ catalysts were in gray-black color, and after reduction both of them turn into deep black. However, after reduction, Ni/Al₂O₃-SiO₂ catalyst was observed to self-ignite in air. That was observed during this catalyst was reduced in fixed bed for BET analysis. The reduced Ni/Al₂O₃-SiO₂ catalyst can ignite the plastic pan in a short time even after enough cool down and release heat when it was placed in glass bottle filled by air. That heat release

will not happen in N₂ atmosphere. That was caused by the H₂ adsorbed on the surface of catalyst pore during reduction process. This H₂ can be released into air and react with O₂ allowing self-ignition to happen. Thus, the reduction process showed always followed by CH₄-N₂ or pure N₂ experiments. If the collection of this after reduction catalyst was required, it should be stored in a glass bottle which was filled by N₂. This stored H₂ can also be released during CH₄ injection experiments.



(a)

(b)



(c)

(d)



(e)

Figure 4.2 Catalysts used in chapter 4 as received and reduced (a. Ni/Al₂O₃-SiO₂ reduced, b. NiO/Al₂O₃-SiO₂, c. Ni/SiO₂ reduced, d. Ni/SiO₂ as received, e. HZSM-5)

The XRD results of catalysts used in this chapter are shown in Figure 4.3 and Figure 4.4. It proved that the Ni/Al₂O₃-SiO₂ catalyst can be well reduced after reduction process in fluidized

bed (which was shown in Chapter 3) reactor and the Ni crystal structure of Ni/Al₂O₃-SiO₂ catalyst was clear and complete, and the XRD signal of HZSM-5 was the same with previous HZSM-5 XRD result shown in literature.^[124] However, the Ni/SiO₂ catalyst do not have a clear signal of Ni. Based on the XRD testing principle, this low Ni signal might cause by two opposite reasons, first, the Ni crystal in Ni/SiO₂ was extremely fine and homogeneous, and the crystal size of Ni was very small which may allow Ni to have an ideal contacting area with reactants during experiment; or second, the Ni crystal in that catalyst was heterogeneous and did not have a clear crystal structure. If that is the case, the XRF result may have large error and the poor crystal structure may affect active function of this catalyst in reactor.

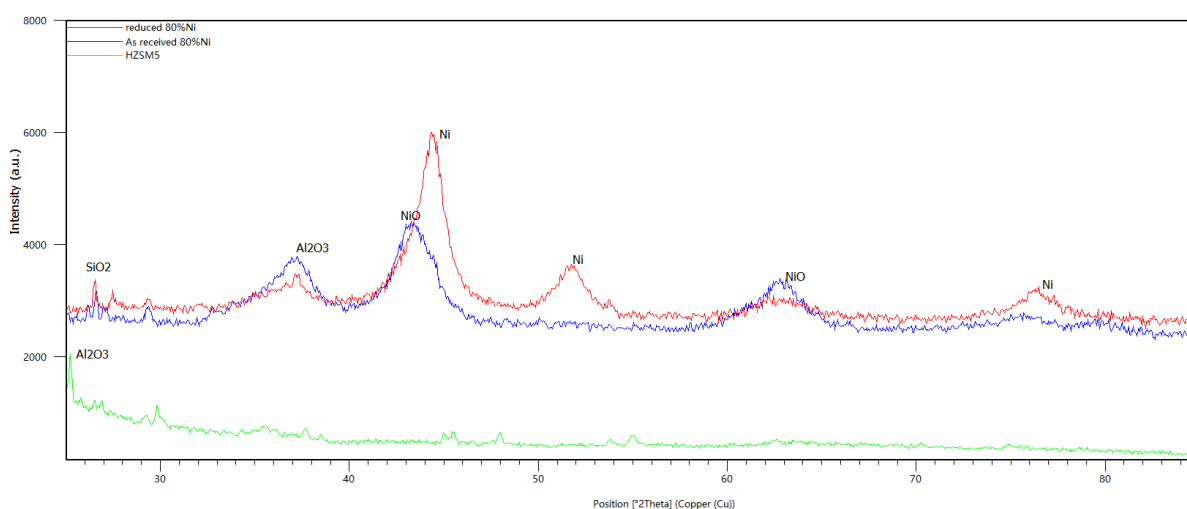


Figure 4.3 XRD patterns of HZSM-5, fresh Ni/Al₂O₃-SiO₂, reduced Ni/Al₂O₃-SiO₂ catalyst.

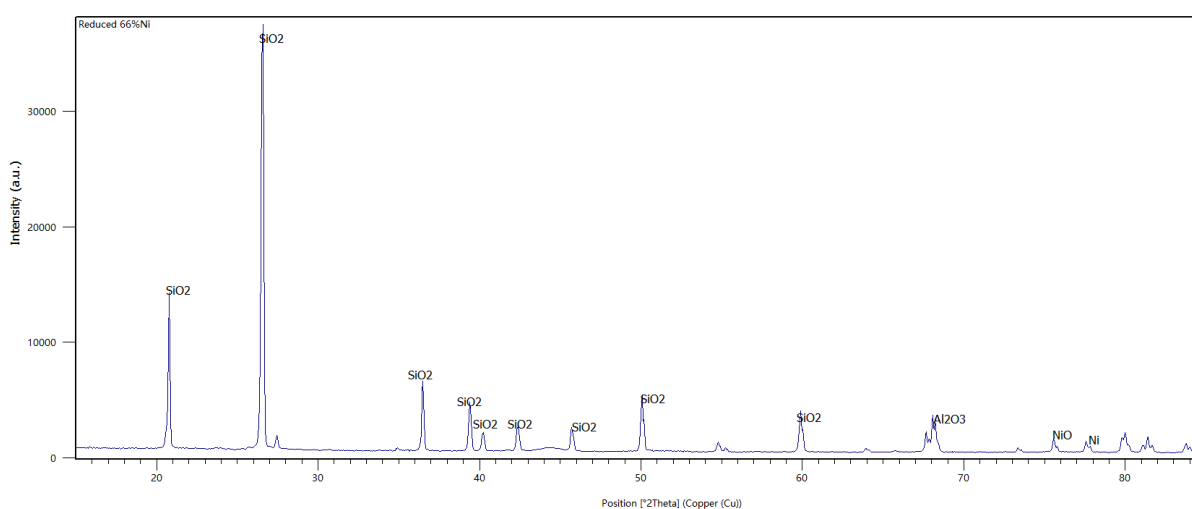


Figure 4.4 XRD patterns of reduced Ni/SiO₂ catalyst

4.3.2 Aspen Simulation for CH₄-only Experiments

A thermodynamic analysis was carried out based to compare the experimental results with equilibrium conditions. A Gibbs reactor was set in Aspen 11.0, and all conditions and gas state were assumed as ideal, which means all gases are set as ideal gas, which followed ideal gas equation of state. As is shown in Table 4.3, CH₄ were first set as input chemical and CH₄, H₂, C₆H₆ and carbon were set as output chemical under temperatures of 550 °C, 600 °C, 650 °C, 700 °C and 1 bar of pressure. The results showed that virtually no C₆H₆ was predicted at equilibrium. Under all reaction conditions, C₆H₆ was not thermodynamically stable respect to cracking into carbon and H₂ and highlights the challenge of operating this system without the methane cracking formation being predominant. Two other simulations used C₆H₆ as input chemical under the same condition with previous simulation. The result proved the assumption that C₆H₆ can completely crack into C and H₂ in these temperatures at equilibrium. Thus, the C₆H₆ need to be removed from reactor in time to avoid being cracked in actual experiment. The gas composition of actual steady state in experiment was different with it in the simulated equilibrium state

Table 4.3 Aspen simulation result of CH₄ or C₆H₆ as only input material

Temperature	Input	Output (mol fraction, %)			
		CH ₄	H ₂	C ₆ H ₆	C
550 °C	CH ₄	27.7	48.2	8.3×10^{-15}	24.1
	C ₆ H ₆	-	33	1.6×10^{-15}	67
	C ₆ H ₆	10.8	18.9	3.6×10^{-16}	70.3
580 °C	CH ₄	44.9	52.4	1.7×10^{-14}	26.2
	C ₆ H ₆	-	33	2.1×10^{-15}	67
	C ₆ H ₆	8.8	21.6	6.6×10^{-16}	69.6
600 °C	CH ₄	17.8	54.8	2.5×10^{-14}	27.4
	C ₆ H ₆	-	33	2.5×10^{-15}	67
	C ₆ H ₆	7.7	23.2	9.7×10^{-16}	69.2
650 °C	CH ₄	11.1	59.3	5.7×10^{-14}	29.6
	C ₆ H ₆	-	33	3.8×10^{-15}	67
	C ₆ H ₆	5.0	26.7	2.1×10^{-15}	68.3
700 °C	CH ₄	6.8	62.2	1.1×10^{-13}	31.1
	C ₆ H ₆	-	33	5.4×10^{-15}	67
	C ₆ H ₆	3.2	29.1	3.8×10^{-15}	67.7

4.3.3 Effect of Different Catalysts

The 700 °C, 5 g Ni/Al₂O₃-SiO₂ catalyst under 30% CH₄ atmosphere, without lignin was chosen as the blank experiment, which was based on the result of a 700 °C, no catalyst, 30% CH₄, without lignin test before formal experiment. This blank experiment showed that only very limited CH₄ can happen DMA reaction under 700 °C without catalyst. Based on previous study did by other researchers (illustrated in Chapter 2), HZSM-5 was chosen to test if it can work on DMA reaction without adding metal site as it was a good catalyst in lignin pyrolysis. Ni/Al₂O₃-SiO₂ and Ni/SiO₂ catalyst were chosen to check the performance of different Ni catalyst on DMA reaction. As is shown in Table 4.4, Ni/Al₂O₃-SiO₂ catalyst obtained best performance on H₂ and oil yields. The HZSM-5 catalyst nearly not catalyzed the reactions without metal site on it. That can be explained by that HZSM-5 catalyst had a low thermal stability and the cracked material lost the catalyzing function (The HZSM-5 can crack lower than 500 °C^[125]), or HZSM-5 cannot catalyze the DMA reaction without metal site. The small difference between the result of Ni/SiO₂ and NiO/SiO₂ experiments showed that both reduced metal and metal oxide can be active DMA and CH₄ cracking reactions. That might because the

NiO itself can be reduced by H_2 generated by CH_4 during experiment. The crystal size and shape of Ni reduced from NiO by in-situ generated H_2 was different with the Ni in other experiment (Run 3) which was reduced by ex-situ H_2 in different reduction temperature. That different on crystal size and shape further caused the different on experiment result.

Table 4.4 Conversion, yields and selectivities obtained in DMA at 700 °C, 30% CH₄, 5 g catalyst experiments

Run	Catalyst and amount	CH ₄ conversion, mol%	H ₂ yield, mol%	Oil yield, wt.%	Oil selectivity, wt.%	Weight loss of catalyst samples on TGA, wt.%	Deposit carbon selectivity, wt.%
1	Ni/Al ₂ O ₃ -SiO ₂	33.6	32.1	12.1	44.1	20.4	51.3
2	HZSM-5	0.51	0.05	0	0	0.3	96.2
3	Ni/SiO ₂	16.4	20.3	1.4	28.7	23.7	65.9
4	NiO/SiO ₂	16.1	17.75	1.2	26.9	25.2	67.3

4.3.4 Effect of CH₄ Concentration and Catalyst Amount

Two different feeding concentrations (30% and 80%) of CH₄ in N₂ as balance gas were used at 700 °C and 1 bar_a to test the effect of CH₄ concentration. As shown in Figure 4.5 (30% CH₄ experiment stopped at 30 min, and 80% CH₄ experiment stopped at 40 min), faster catalyst deactivation took place in experiments with 80% inlet CH₄ concentration, where H₂ concentration dropped markedly in the first 10 min to reach a steady state value of 26 vol.%. On the other hand, this initial deactivation was slower in 30% CH₄ experiments and H₂ concentration stabilized after a time on stream (TOS) of 30 min at around 10 vol.%.

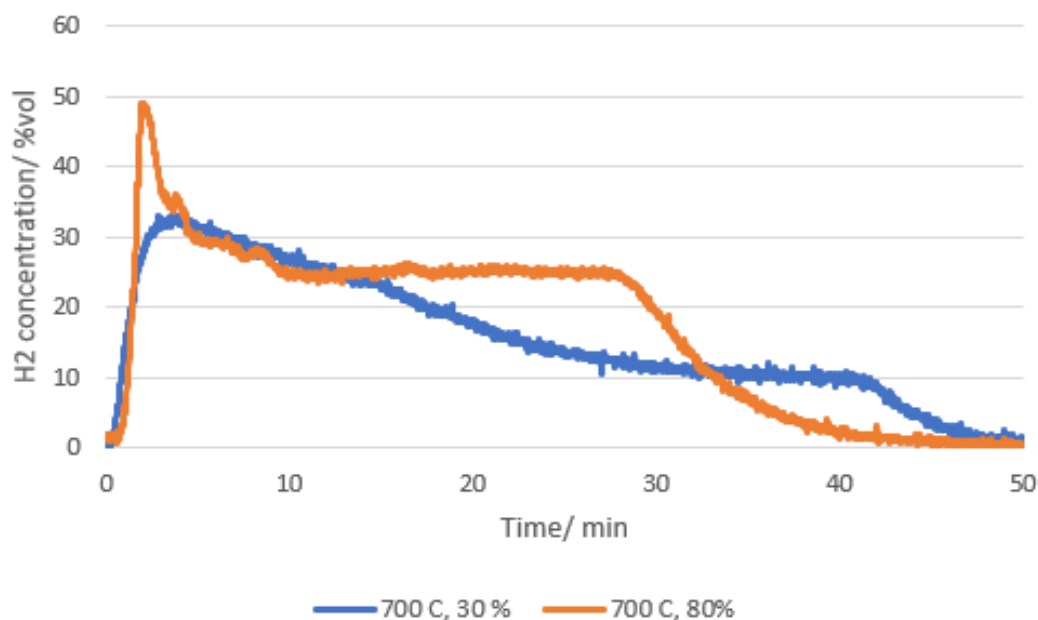


Figure 4.5 H₂ concentration in the products as a function of time on stream for DMA under 700 °C, 1 bar, 2 L min⁻¹ total gas flow rate, 60 g sand and Ni/Al₂O₃-SiO₂ as catalyst as feedstock. CH₄ conversion was larger at the lower CH₄ concentration (Table 4.5) and H₂ yields decreased from 32.1 to 24.7% with the increase in CH₄ from 30 to 80 vol.% as a result of the greater catalyst deactivation. Oil yields also decreased when the higher CH₄ concentration was employed. The weight yields of oil and mol yields of H₂ matched DMA stoichiometric proportions at 30% CH₄, indicating predominance of the DMA reaction, while the H₂ yield was higher than expected from the oil yield at 80% CH₄, pointing to greater extent of CH₄ pyrolysis. This explains that the H₂ concentration ratio between the experiments with the two CH₄ concentrations (2.6) was higher than the expected value (1.9) calculated taking into

consideration the conversions achieved in both experiments. This was further confirmed by the greater carbon formation on the catalyst measured by TGA analysis (Table 4.5). As a high H_2 concentration in the fluidized bed is desirable in order to promote lignin depolymerization, further experiments were performed at 80% feed CH_4 concentration. As discussed below, the deactivation and lower yield were to be overcome by a decrease in temperature as part of the optimization of process conditions.

The influence of the amount of catalyst mixed with bed material was also tested in this study. Two experiments were performed using different catalyst amounts, 1.56 g and 5 g, under 700 °C and 80% CH_4 atmosphere. The amount of catalyst did not provide a large difference in fluidization conditions as the total bed weight difference was small when considered the 60 g bed material and did not change the bed length. As is shown in Table 4.5, significantly higher CH_4 conversion, H_2 concentration and oil yield were observed when using 5 g of catalyst (24.7 mol% and 8.0 wt.%) than those in the experiment with 1.56 g of catalyst (4.8 mol% and 3.9 wt.%). The average reaction rate in the bed was also larger ($0.019 \text{ mol } CH_4 \text{ min}^{-1} \text{ g}^{-1}$ in 1.56 g catalyst vs. $0.031 \text{ mol } CH_4 \text{ min}^{-1} \text{ g}^{-1}$ in 5 g catalyst) in the experiment with 5 g, which suggests some by-pass of the catalytic bed may have taken place in the fluidized bed due to the small catalyst loading. The experimental loss of catalyst cannot be avoided during fluidization experiments. The catalyst can lose when the gas change from H_2 to CH_4 , temperature change which made gas flow rate in reactor increase, normal lose/leak out from quartz linear. This minor lost will not affect 5 g catalyst experiment too much for it still had enough catalyst stayed in fluidized bed. But, in 1.56 g catalyst experiment, this catalyst lost cannot be ignored.

Table 4.5 Conversion, yields and selectivities obtained in DMA at different concentration and catalyst amount experiments

Temperature, (°C)	Feedstock CH ₄ Concentration (%)	Catalyst and amount	CH ₄ conversion, mol%	H ₂ yield, mol%	Oil yield, wt.%	Oil selectivity, wt.%	Weight loss of catalyst samples on TGA, wt.%	Deposit carbon selectivity, wt.%
700	30% CH ₄	5 g, Ni/Al ₂ O ₃ - SiO ₂	33.6	32.1	12.1	44.1	20.4	51.3
700	80% CH ₄	5 g, Ni/Al ₂ O ₃ - SiO ₂	22.5	24.7	8.0	41.5	36.7	58.1
700	80% CH ₄	1.56 g, Ni/Al ₂ O ₃ - SiO ₂	4.4	4.8	3.9	95.6	0.5	1.0

4.3.5 Effect of Temperature and Catalyst Reduction on DMA

The H₂ concentration in the product gas was measured as a function of TOS at several temperatures as shown in Figure 4.6. The DMA reaction was carried out with a feed composed of 80% CH₄ and with 5 g of Ni/Al₂O₃-SiO₂ as catalyst, based on the most favourable conditions to obtain a higher H₂ concentration as identified in the previous section. Experiments were performed between 550 °C, the threshold temperature that allows DMA reaction to happen,^[126] and 700 °C to observe the catalyst deactivation rate and to find the optimal conditions for H₂ and oil generation. As can be seen from Figure 4.6, temperature plays an important role in H₂ generation, which tends to increase as reaction temperature increases. However, catalyst deactivation was fast at 650 and 700 °C, with the H₂ production reaching its highest level within the first 2 min on stream and then decaying, leading to a steady state H₂ concentration lower than that achieved at 600 °C. It therefore seems that a reaction temperature of around 600 °C would be the optimal. However, as discussed in Chapter 3, due to the need to avoid blockages when feeding lignin, a slightly lower temperature of 580 °C was applied to simultaneous pyrolysis experiments, whose results are presented in subsequent chapters. This temperature led to an only slightly lower H₂ concentration than observed at 600 °C. The test showed that steady state could be sustained without any apparent catalyst deactivation for over 40 min on stream (a slightly longer TOS also applied to lignin conversion experiments), as shown in Figure 4.6.

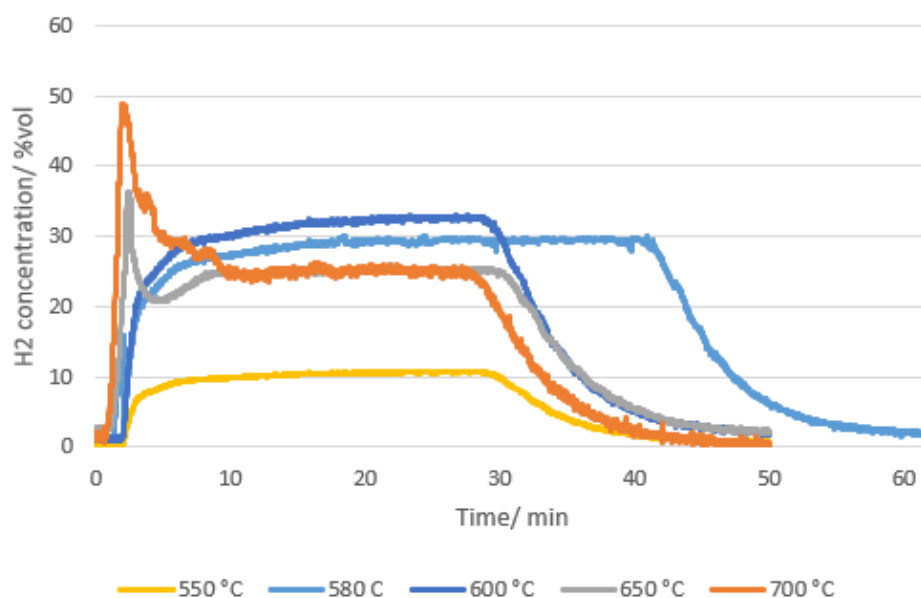


Figure 4.6 H₂ concentration in the products as a function of time on stream for DMA in 1 bar, 2 L min⁻¹ total gas flow rate, 80% CH₄ atmosphere and 5 g Ni/Al₂O₃-SiO₂ as catalyst mixed with 60 g sand bed material. A longer TOS of over 40 min was applied to the reaction at 580 °C while for the others it was 30 min.

H₂ concentration and oil yields at steady state as a function of temperature are shown in Table 4.6. Both peaked at 600 °C as the catalyst kept its activity for the whole experiment at this temperature. H₂ yield was 29.7 mol%, a value close to 32.1 mol% that observed at 700 °C with 30% CH₄ at the inlet (Table 4.5), showing that although the peak H₂ concentration is higher in high temperature, using a lower temperature can overcome the decrease in yield due to deactivation at the higher CH₄ concentration.

An experiment was carried out at 600 °C and 80% CH₄ atmosphere in the feed to assess the effect of pre-reduction of the NiO/Al₂O₃-SiO₂ catalyst (results shown in Table 4.6). NiO without reduction did not have an obvious difference with reduced Ni on H₂ generation, but the latter led to a higher oil yield. This suggests reduced Ni catalyst had a higher catalytic activity on DMA reaction and NiO had a higher catalytic activity on CH₄ cracking to form hydrogen and carbon on the catalyst according to CH₄ cracking. This was confirmed by measurements of carbon deposits on the catalysts, which were carried out after each experiment and are shown in Table 4.6. As discussed in section 4.3.3, the NiO can be reduced during experiment by H₂ generated by CH₄ cracking. This process can only generate carbon and H₂

before enough Ni was generated to allow DMA reaction to become dominated reaction. And that could be the reason why the carbon yield was higher in NiO reaction. These tests also indicated that carbon did not deposit on sand.

The carbon deposit generated from CH₄ cracking was the key reason for catalyst fast deactivation, being very high for reaction temperatures above 600 °C where a significant drop in H₂ production was observed during the runs. As is shown in Table 4.6, the CH₄ conversion had the same trend as H₂ and oil yields, reaching its highest steady state level at 600 °C with reduced Ni/Al₂O₃-SiO₂ as catalyst.

Table 4.6 Conversion, yields and selectivities obtained in DMA at different temperature and catalyst reduction experiments

Temperature, (°C)	Feedstock CH ₄ Concentration (%)	Catalyst and amount	CH ₄ conversion, mol%	H ₂ yield, mol%	Oil yield, wt.%	Oil selectivity, wt.%	Weight loss of catalyst samples on TGA, wt.%	Deposit carbon selectivity, wt.%
550	80% CH ₄	5 g, Ni/Al ₂ O ₃ - SiO ₂	12.1	9.7	0.83	17.3	25.7	82.1
580	80% CH ₄	5 g, Ni/Al ₂ O ₃ - SiO ₂	33.2	21.2	12.1	59.2	5.8	39.4
	30% CH ₄	5 g, Ni/Al ₂ O ₃ - SiO ₂	32.5	28.9	9.2	52.8	6.4	42.6
600	80% CH ₄	5 g, Ni/Al ₂ O ₃ - SiO ₂	35.8	29.7	16.9	66.1	5.2	27.3
		5 g, NiO/Al ₂ O ₃ - SiO ₂	30.4	29.5	13.2	49.7	33.7	47.1
650	80% CH ₄	5 g, Ni/Al ₂ O ₃ - SiO ₂	21.5	23.5	7.9	44.9	28.5	54.0
700	80% CH ₄	5 g, Ni/Al ₂ O ₃ - SiO ₂	22.5	24.7	8.0	41.5	36.7	58.1

DMA was the dominant reaction at 580 °C and 600 °C, but CH₄ cracking increased significantly at 650 °C and 700 °C, which caused fast catalyst deactivation. This was reflected in the oil selectivity values, which reached their peaks at 600 °C in experiments with 80% CH₄ and 5 g Ni/Al₂O₃-SiO₂ catalyst (Table 4.6), and dropped by about one-half at higher temperatures. A high oil selectivity was observed at 700 °C with 1.56 g of catalyst. However, it is thought that most catalyst was by-passed in that experiment, as only very limited CH₄ reacted (conversion was 4.4%) and formed deposits on the catalyst surface. On the other hand, oil selectivity was very low and carbon selectivity was at its highest in the 550 °C experiment, as the DMA reaction only took place to a limited extent at that relatively low temperature, near the threshold for DMA to be observed.

In 600 °C temperature experiment, the Ni/Al₂O₃-SiO₂ and NiO/Al₂O₃-SiO₂ catalyst had an obvious different when compared with Ni/SiO₂ performance under 700 °C. As is shown in Table 4.6, Ni/Al₂O₃-SiO₂ can generate less carbon (27.3 wt.% deposit carbon selectivity) than NiO/Al₂O₃-SiO₂ (47.1 wt.%). That showed metallic oxide preferentially catalyses CH₄ cracking than DMA, while reduced metal exhibits the opposite performance.

The results discussed above have shown that the most promising conditions for generation of H₂ and oil are around 600 °C and 80% CH₄ atmosphere with 5 g Ni/Al₂O₃-SiO₂ catalyst. This condition also had a comparatively high oil and low carbon deposit selectivities, while the catalyst was observed to retain its initial activity during the experiments. As mentioned in the Experimental section, lignin was pretreated by mild oxidation to avoid blockages in the feeding line to the fluidized bed, which occurred in initial tests. This pretreatment avoided operability issues when temperature was below 620 °C. To provide a safe operating temperature difference, experiments co-feeding lignin and CH₄ were carried out at 580 °C, well below this threshold. When compared with the DMA results at 600 °C and 80% CH₄, the 580 °C and 80% CH₄ experiment had a lower H₂ and oil yield and oil selectivity (Table 4.6). Neither temperature led to significant catalyst deactivation. On the other hand, the experiment at 580 °C and 80% CH₄ had a higher oil yield and oil selectivity, but a lower H₂ yield than that at the same temperature and 30% CH₄. This trend was different from that observed at 700 °C (which had a higher oil yield and selectivity under 30% CH₄ condition). This is because catalyst deactivation was fast at 700 °C and the higher CH₄ concentration generated more carbon deposit, leading to catalyst

deactivation in a shorter time than the lower CH₄ concentration. This faster deactivation led to a lower selectivity to oil as CH₄ pyrolysis replaced DMA to become the dominant reaction. On the other hand, this was not the case under 580 °C in both 80% CH₄ and 30% CH₄ conditions, as catalyst deactivation did not obviously happen. The results of 580 °C experiments showed that the higher CH₄ concentration improved the DMA selectivity.

4.3.6 Structure of Carbon Generated on the Catalyst

According to previous research, CH₄ can generate both agglomerated particle shape and nano-fiber shape carbon based on different catalyst preparation process and experiment environment.^[161] If the carbon generated on the catalyst can fluently move from one side of catalyst surface to another side, the carbon nano-fiber can be allowed to generate, otherwise the deposit carbon will agglomerated on the midway of catalyst surface and finally accumulated into particle shape carbon, which deactivate the catalyst fast.^[160,161]

As is shown in the SEM micrographs in Figure 4.7, the reduced Ni/Al₂O₃-SiO₂ catalyst before DMA experiments did not have carbon particle or nanofibers on its surface. This fresh reduced catalyst had a multi-porosity and multilayer structure. The SEM of the catalyst recovered from the 700 °C and 80% CH₄ DMA experiment, illustrated in Figure 4.8, there is a limited carbon nanofiber presence, but the main deposit was amorphous carbon, which covered the Ni/Al₂O₃-SiO₂ catalyst surface. This caused the catalyst deactivation observed in these high temperature experiments. On the other hand, in the spent catalyst recovered from the experiment at 600 °C and 80% CH₄, mainly carbon nanofibers can be observed by SEM (shown in Figure 4.9), although these did not cover the catalyst surface. These nanofibers grew mostly in the direction perpendicular to the catalyst surface. That means the process, used H₂ to in-situ reduce catalyst in fluidized bed and directly switch the gas from H₂ to CH₄, used in this experiment can help to generate carbon nano fiber and 600 °C was a condition favor to generate carbon nano fiber. According to literature, suitable H₂ concentration in reactor is the key to guide CH₄ to generate CNF. The experiment with in-situ reduce can make sure reactor have enough H₂ at the very beginning of CH₄ enter. And CH₄ can be directly converted into CNF. When compare the result of Ni and NiO at 600 C in Table 4.5. Ni had 27.3% carbon selectivity and NiO had 47.1%

which is much higher. As mentioned above in the discussion of Figure 4.6, catalyst deactivation under these conditions was not observed. In addition to the smaller amounts of deposits, the carbon nanofibers, which were the predominant carbon form at 550 °C, 580 °C and 600 °C, may have allowed for a more open structure than the carbon deposited at 650 °C and 700 °C, still enabling CH₄ to access the catalyst porosity and sustain catalytic activity.

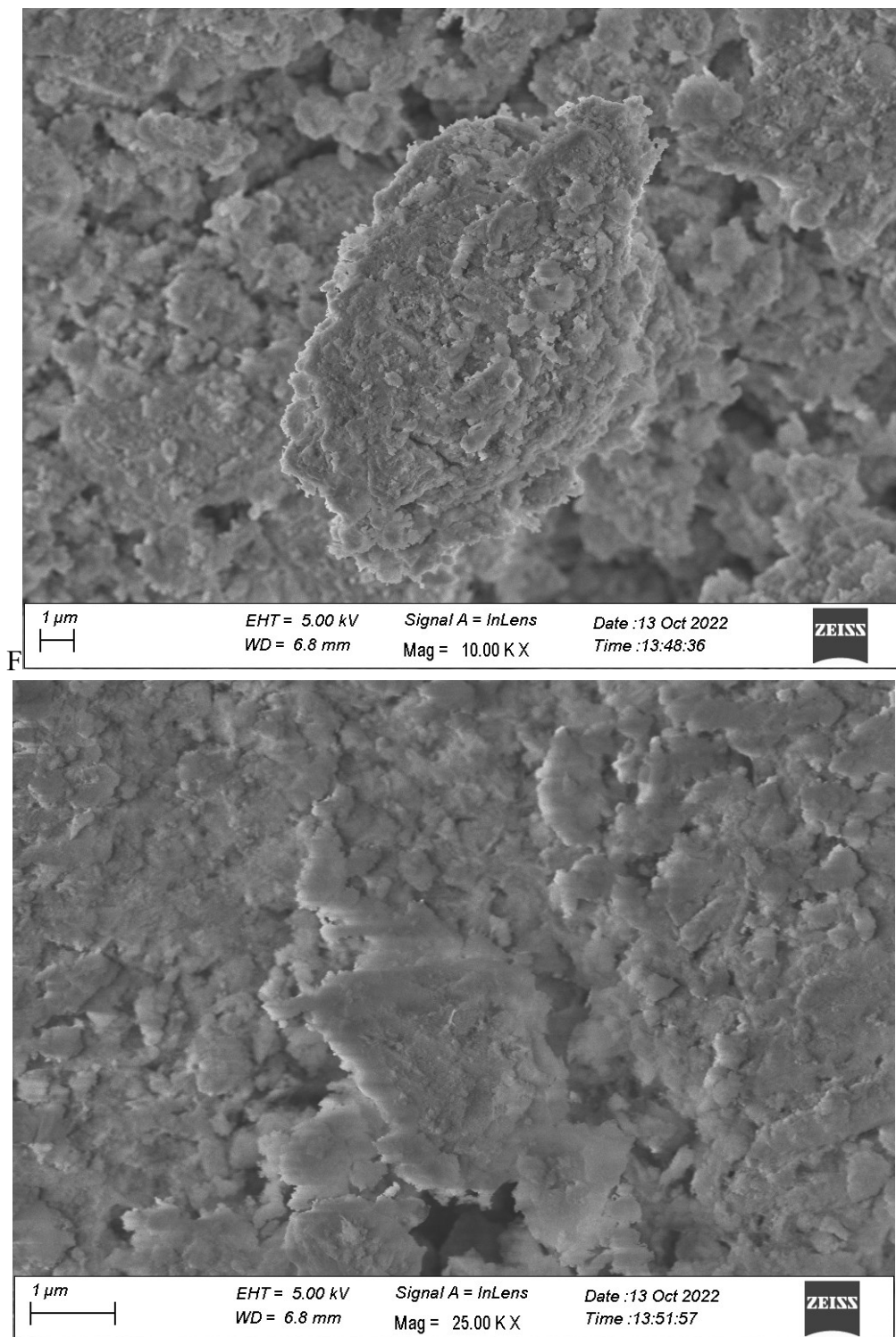
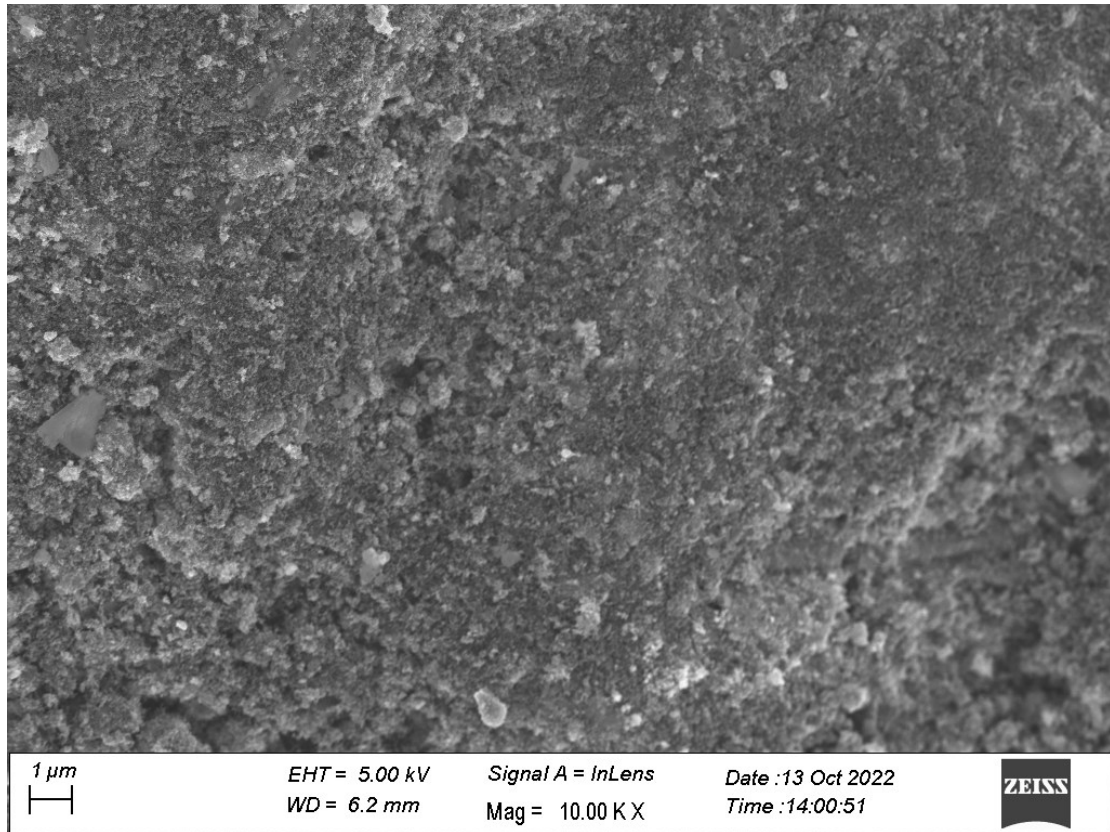


Figure 4.7 SEM image of fresh Ni/Al₂O₃-SiO₂ catalyst



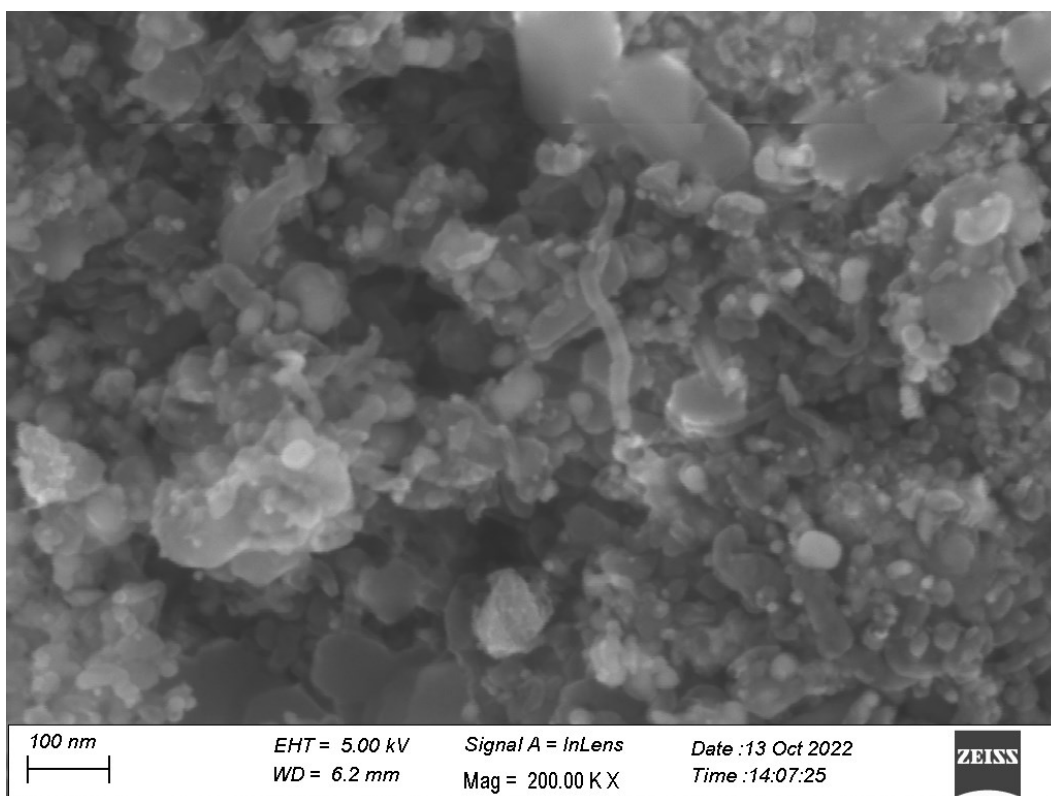
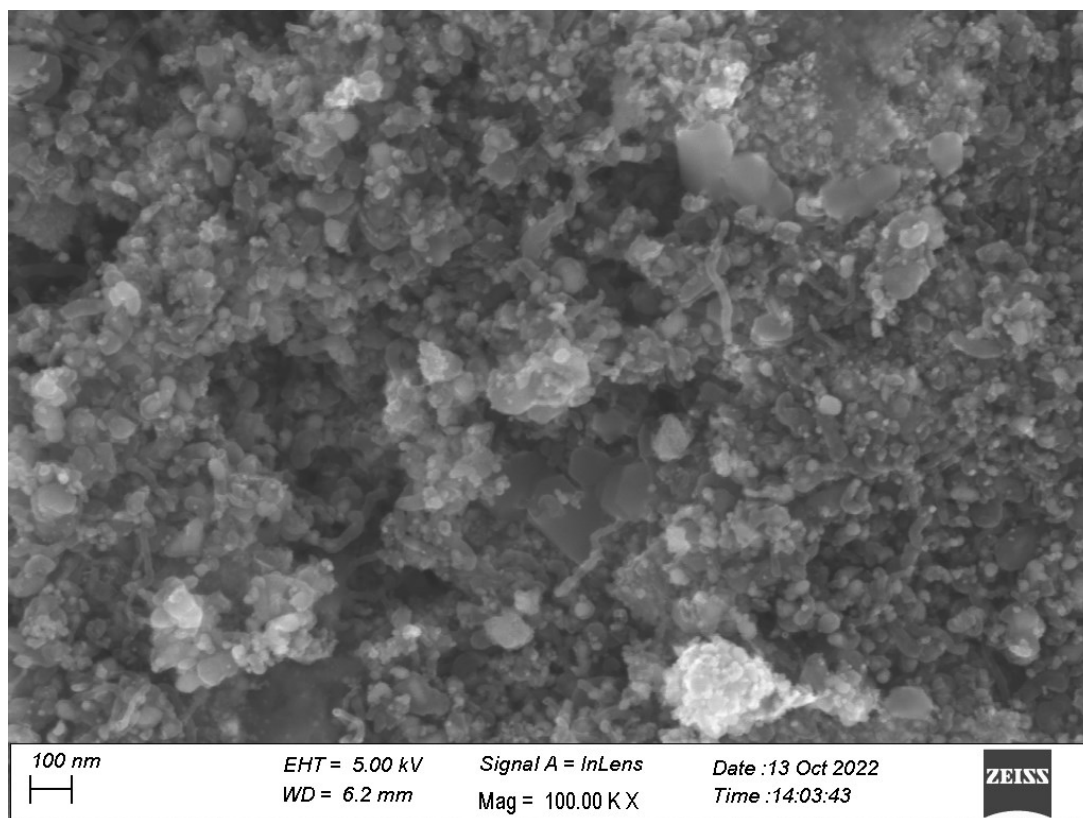
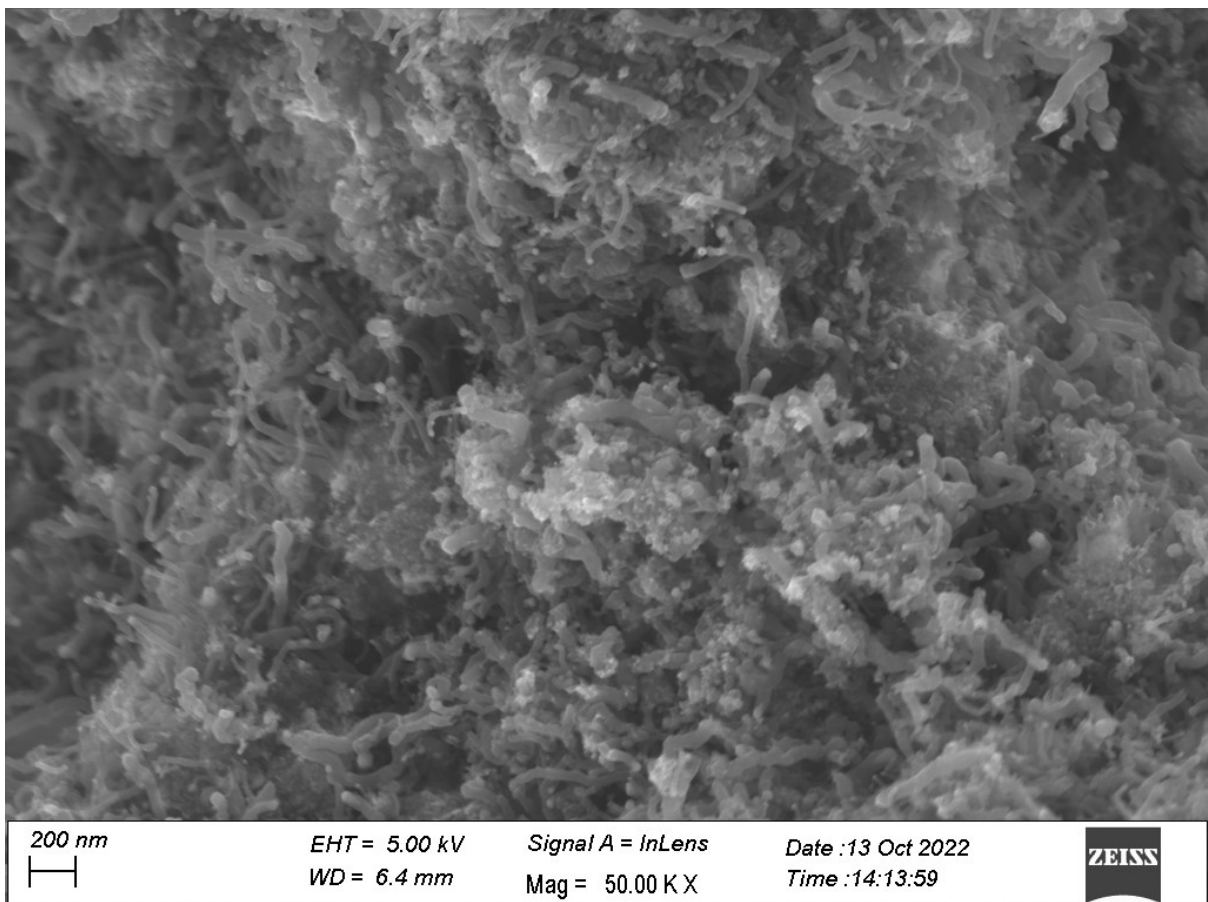
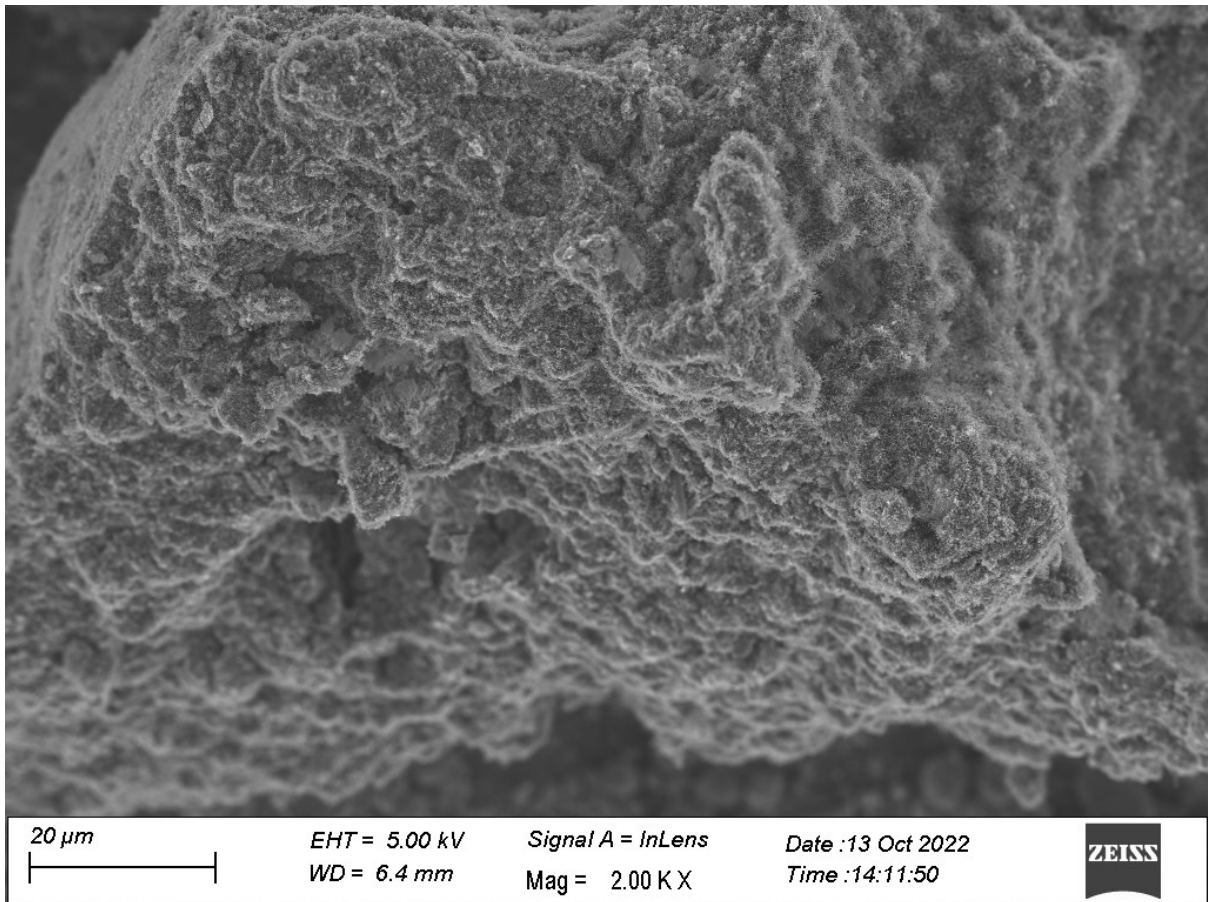


Figure 4.8 SEM image of Ni/Al₂O₃-SiO₂ catalyst after 700 °C, 80% CH₄ experiment.



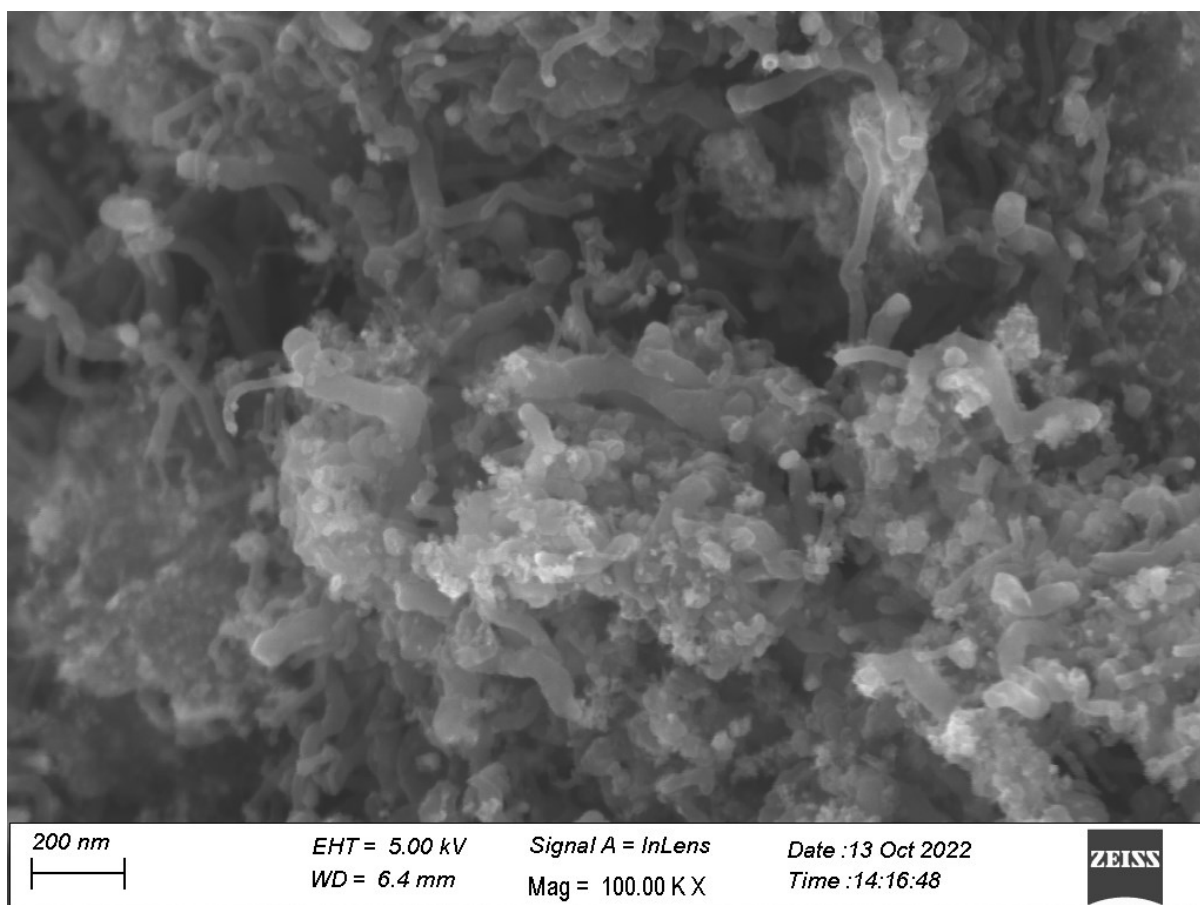


Figure 4.9 SEM image of Ni/Al₂O₃-SiO₂ catalyst after 580 °C, 80% CH₄ experiment

4.4 Conclusions

In Aspen simulation, nearly all benzene can be cracked into H₂ and C after long-enough steady state. That was because benzene is not stable under temperature higher than 550 °C. To avoid the benzene was fully cracked in experiment, the continuously gas was used to bring the generated oil out from reactor in time which can break the equilibrium. That can be used to overcome the equilibrium limitation.

Based on that, an optimal condition of CH₄ to generate H₂ and oil was determined at 600 °C, 80% CH₄ and 5 g Ni/Al₂O₃-SiO₂ catalyst. This temperature and catalyst reduction process operated in fluidized bed reactor before experiment help to keep reactor in a H₂ atmosphere, this initial H₂ atmosphere can guide carbon generated by CH₄ to grow in carbon nanofiber structure rather than carbon particle. This extremely slowed the speed of carbon full covered the surface of catalyst and allowed the catalyst limited deactivated during experiment. The H₂

and oil generation yield were first increased from 9.7 mol% and 0.83 wt.% under 550 °C to 29.7 mol% and 16.9 wt.% under 600 °C and then continuously decreased to 24.7 mol% and 8.0 wt.% in 700 °C. Based on Aspen simulation, CH₄ only reactions can generate more H₂ and oil under higher temperature, although nearly all benzene cracked into C and H₂, high temperature can allow more benzene left. However, according to the comparison of SEM results of 600 °C and 700 °C experiment, the high temperature can also make deposit carbon to generate in particle shape. This particle shape deposit carbon covered on the surface of Ni and prevent Ni to contact with CH₄. That will deactivate the Ni catalyst which finally reduced the H₂ and oil yields. The temperature can also affect the operation. Based on the agglomeration avoidance tests which will be discussed in Chapter 5, 600 °C can made lignin pyrolysis experiment operated under an unstable condition. Thus, the optimal temperature was chosen as 580 °C. All other potential variables that can affect the H₂ and oil yield during CH₄-only experiments have been experimentally studied.

- (1) The results obtained from different catalyst experiments showed that the HZSM-5 catalyst used in this study cannot active the DMA reaction without metal site loaded. That was because it was unstable under high temperature or HZSM-5 do not have catalyzing function for DMA reaction under this temperature. The Ni/SiO₂ catalyst had an obviously lower H₂ (20.3 mol%) and oil (1.4 wt.%) yield than Ni/Al₂O₃-SiO₂ catalyst (32.1 mol% and 12.1 wt.% separately). That was because Ni/Al₂O₃-SiO₂ catalyst had much larger surface area, pore size, clear Ni crystal structure. The experiment based on NiO catalyst proved that both DMA and CH₄ cracking reactions can be activated by NiO. When compared with Ni catalyst after reduction, the NiO can generate more deposit carbon, nearly the same level H₂ and less oil.
- (2) Based on BET, SEC results and previous literature,^[127] the main reason caused catalyst deactivation is that the carbon generated by CH₄ can cover the surface of Ni catalyst in a short time. Method that can be used to slow this catalyst deactivation was control the temperature and initial H₂ concentration in reactor to guide the deposit carbon to growth in carbon nanofiber shape.
- (3) In CH₄ concentration experiments, the catalyst deactivation rate was slower under 30% CH₄ than 80% CH₄, which was because higher CH₄ concentration in the same inlet gas flow

rate means more mole CH_4 joined into reaction at the same time and the mole of deposit carbon also increased. That deposit carbon made catalyst deactivated in shorter time than under lower CH_4 concentration. Because of this deactivation of catalyst, the CH_4 conversion, H_2 yield and oil yield of 80% CH_4 experiment were lower than 30% CH_4 experiment.

- (4) The catalyst amount experiment did in this chapter cannot be used to make a conclusion. The experimental loss of catalyst cannot be ignored in 1.56 g catalyst experiment, which made the H_2 and oil yield of 1.56 g catalyst experiment at extremely low level. This guided the experiment design in lignin and CH_4 simultaneous pyrolysis experiments.
- (5) The temperature was the main variables that influence the H_2 and oil yield when catalyst was the same. The temperature lower than 600 °C can guide deposit carbon to growth in carbon nanofiber shape. Only very limited catalyst deactivated after 30 mins 600 °C experiments, according to H_2 in-time curve. And the DMA reaction is relatively stable between 580 °C to 600 °C. That allows 580 °C to be chosen as the optimal temperature in further lignin and CH_4 simultaneous pyrolysis experiment.

Chapter 5. Simultaneous Catalytic Conversion of Lignin and CH₄

5.1 Introduction

Following the experiments described in Chapter 4, a condition of temperature, CH₄ concentration and catalyst favorable to generate H₂ and monoaromatics from methane while keeping carbon formation under control in the fluidized bed reactor has been found. Based on that initial screening, the use of in-situ generated H₂ in lignin upgraded was investigated. The target products of lignin pyrolysis are oil, especially BTEX and other light high added-value chemicals. H₂ is a beneficial gas in lignin pyrolysis and can increase the oil yield and BTEX yield^[73, 74, 75]. However, the effect of in-situ generated H₂ and the simultaneous presence of CH₄ in the reactor need to be studied.

This chapter is divided into five sections in addition to this introduction, which are used to describe and discuss experiments carried out the lignin and CH₄ simultaneous pyrolysis. The experimental conditions are listed in Section 5.2. Section 5.3 illustrates the agglomeration problem happening in the reactor when feeding lignin, its causes and the strategy applied to solve this problem. Section 5.4 discusses the effect of different operating parameters on the oil yield. Finally, summary and conclusions are presented in Section 5.5.

5.2 Experimental Conditions

The fluidized bed reactor introduced in Chapter 3 and used in experiments described in Chapter 4 was used in work with lignin and CH₄ simultaneous pyrolysis. The solid feedstock feeding system used in this chapter was illustrated in Chapter 3. Several test runs were performed to find the conditions in which lignin can be fed smoothly into the fluidized bed. Results from lignin and CH₄ simultaneous pyrolysis experiments were compared with those running a supply of external H₂ to find out whether in-situ H₂ can improve oil yields, and no H₂ (or CH₄ feed) to elucidate the contribution from lignin pyrolysis.

After comparison experiments on the H₂ source, the experiment under 580 °C, 1 bar, 30% CH₄, 5 g Ni/Al₂O₃-SiO₂ catalyst, 1.5 g min⁻¹ feedstock feeding rate, 2 L min⁻¹ and sand : lignin = 3:1

dilution rate was chosen as initial experiment for further research. After testing every variable, the best condition of this variable was set as the new base condition for this variable in future experiment (as is shown in Table 5.1).

The influence of temperature was set in range of 560 °C, the lowest temperature that allows DMA to happen according to results introduced in Chapter 4, to 620 °C, the feeding rate and feedstock dilution ratio (sand to lignin ratio) were two relevant variables used to calculate the amount of lignin that entered the reactor per unit of time. Based on the experience in Chapter 4, the catalyst amount was kept between 3.5 g and 5 g. The total inlet gas flow rate was used to test the influence of lignin (which cannot completely react and some of them can be brought out from reactor by gas) and volatiles residence time in the reactor. The influence of pressure was considered worth to be tested as high pressure could be beneficial to the hydrocracking/hydrodeoxygenation reactions undergone by lignin, but it can also reduce the H₂ and benzene generated by the DMA reaction. In the final experiment, the high level 80% CH₄ experiment was done to find the influence of methane concentration. As mentioned in Chapter 3, lignin was pretreated by mild oxidation to avoid blockages in the feed to the fluidized bed, which occurred in initial tests. This pretreatment avoided operability issues provided temperature was below 620 °C. To provide a safe operating temperature difference, experiments co-feeding lignin and CH₄ were carried out at 580 °C, well below this threshold. The experiment was first run under 30% CH₄ atmosphere to control the influence of CH₄ on the result in a low level for experiments changed other variables. The calculation equations used in this chapter were shown in Chapter 3. (Equation 3.12, 3.13, 3.17, 3.18)

The list of experiments with their corresponding conditions is given in Table 5.1.

Table 5.1 Experimental conditions

Run	Temperature (°C)	Pressure (bar)	Gas flow rate (L min ⁻¹)	Catalyst	Feedstock feeding rate (g min ⁻¹)	Feedstock dilution ratio*	CH ₄ concentration (%)	H ₂ source
1	580	1	2	/	1.5	Sand: lignin=3:1	0	/
2	580	1	2	5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=3:1	0	/
3	580	1	2	5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=3:1	0	External 15.4%
4	580	1	2	5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=3:1	30	In-situ from CH ₄
5	560	1	2	5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=3:1	30	In-situ from CH ₄
6	600	1	2	5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=3:1	30	In-situ from CH ₄
7	620	1	2	5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=3:1	30	In-situ from CH ₄
8	580	1	2	5g, Ni/Al ₂ O ₃ - SiO ₂	0.7	Sand: lignin=3:1	30	In-situ from CH ₄
9	580	1	2	5g, Ni/Al ₂ O ₃ - SiO ₂	2	Sand: lignin=3:1	30	In-situ from CH ₄
10	580	1	2	5g, Ni/Al ₂ O ₃ - SiO ₂	2.5	Sand: lignin=3:1	30	In-situ from CH ₄
11	580	1	2	3.5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=3:1	30	In-situ from CH ₄

Run	Temperature (°C)	Pressure (bar)	Gas flow rate (L min ⁻¹)	Catalyst	Feedstock feeding rate (g min ⁻¹)	Feedstock dilution ratio*	CH ₄ concentration (%)	H ₂ source
12	580	1	1.6	5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=3:1	30	In-situ from CH ₄
13	580	1	1.15	5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=3:1	30	In-situ from CH ₄
14	580	1	1.15	5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=2:1	30	In-situ from CH ₄
15	580	1	1.15	5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=1.5:1	30	In-situ from CH ₄
16	580	3	1.15	5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=1.5:1	30	In-situ from CH ₄
17	580	5	1.15	5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=1.5:1	30	In-situ from CH ₄
18	580	1	1.15	5g, Ni/Al ₂ O ₃ - SiO ₂	1.5	Sand: lignin=1.5:1	80	In-situ from CH ₄

*The lignin in this table means pre-oxidated lignin.

5.3 Lignin Feeding Tests and Agglomeration Avoidance

The agglomeration of lignin and sand was an inevitable problem that happened in the fluidized bed reactor. Agglomerates can be comprised of all or some of bed material, catalyst and lignin. The temperature at which KL begins to pyrolyse is around 300 °C^[115]. As shown in Chapter 3, the lignin is heated in the feeding and spout line before it enters the quartz liner. That means lignin pyrolysis has begun to happen in the spout line with the generation of a viscous oil. This oil made lignin very easy to stick together and generate larger particle size agglomerated material, which can then block the spout line.

Agglomeration can also happen and cause blockage in the reactor itself. When the agglomerates material had a higher minimum fluidization gas flow rate than the actual inlet gas flow rate, the agglomerated material was observed to drop down to the bottom of quartz liner. The accumulation of these large particles would finally cover the outlet spout line opening and stop the experiment. Thus, finding methods that can mitigate these agglomeration and blockage problems became an important operating issue before experiments could be conducted.

In experiments carried out to determine feasible KL feeding conditions, the cylinder regulator outlet pressure was set at 2 bar and the pressure of reactor measured by pressure gauge at the bottom (pressure gauge P3 shown in Chapter 3) of reactor was between 0.1 to 0.2 bar when the bed material was fluidizing and 0.2 to 0.3 bar when the feedstock was fed into the reactor, which was because feedstock can touch and hit the wall of tube when flowed in spout line and that would increase the pressure losses along the tube. Testing experiment showed that the reactor pressure increased when the agglomeration material accumulated in spout line or reactor. If the reactor pressure reaches 1.7 bar, the feedstock and gas cannot flow smoothly into the reactor, and the indication number on gas flow controller begins to fast decrease to zero which means no gas can be flow from cylinder to reactor system. For safety reasons, this pressure was not allowed to go over 1.7 bar and the reactor was considered fully blocked at this condition. The time at which the gauge pressure reached 1.7 bar was taken as an indicator of how severe the blockage problem was. If this time was longer than 40 min, the conditions applied are feasible and it would meet requirements for a full experiment to be performed.

To solve this agglomeration and blockage problem, several parameters were tested which include feeding rate of feedstock, inlet gas flow rate, sand dilution rate of lignin, methane concentration, catalyst introducing, temperature, pre-treatment method (pre-dry, torrefaction, pre-oxidation), volatile content and ash content. The result of blockage experiments is shown in Table 5.2. The main finding from these experiments was that the introduction of catalyst and pre-treatment method can significantly influence the time before blockage happens.

According to results shown in Table 5.2, the feedstock feeding rate was first tested to determine if the amount of lignin entered the reactor can affect the blockage speed, according to initial assumption, more lignin can generate more large particle agglomeration material at the same time than less lignin. The result showed that low feedstock feeding rate can help to extend the time before blockage. However, even the feedstock feeding rate reached 0.7 g min^{-1} (the motor in feeding system can only work stably higher than this condition), the time before blockage was still too short (2 min 25 s) for simultaneous pyrolysis experiments. The gas flow rate was tested to check the influence of lignin and volatile residence time to the time before blockage. This influence was also relatively small which had longest 3 min 13 s experiment time before blockage, which was still not available to use in formal experiments. The first important variable that can help to obviously improve the situation in blockage problem was dilution ratio. The KL was mixed with sand in a ratio of 1:1 and 1.5:1. The time before blockage under 1.5:1 condition was long enough (longer than 40 min) for KL and CH_4 simultaneous pyrolysis experiments. That can be explained by: firstly, dilution by thermal stable sand can further decrease the KL feeding rate which allows less KL to enter reactor in every minute; secondly, sand was not sticky like KL and initial products generated by KL, which made KL diluted by sand was not easy to touch with other sticky material and the happen of agglomeration can be avoid in spout line. After dilution ratio experiments finished, two low level CH_4 (4% and 30%) included experiments were tested which proved 1.5:1 feedstock dilution ratio can meet the requirements of operation.

However, when $\text{Ni/Al}_2\text{O}_3\text{-SiO}_2$ catalyst was added into reactor, the system was blocked in a short time again. At that case, agglomeration and blockage mainly happened at the end of spout line and in the reactor. That was because catalyst become a new high density source of bed material agglomeration. Previous research also found that in CH_4 atmosphere Ni-based catalyst

itself was easy to agglomerate with bed material and feedstock. Among that catalyst, the Ni-catalyst supported with SiO_2 can importantly agglomerated with each other.^[161] In order to solve this problem, the dilution rate was further changed to sand:lignin = 3:1, but 3:1 dilution ratio still had a short time before blockage (3 min 39 s). And that is why tests moved to check if reducing reactor temperature can help to solve problem. Although reducing reactor temperature to 500 °C can allow the system to work for 11 min 9 s, but 500 °C cannot induce DMA reaction. Another high ash content KL from China was also tested under 600 °C with 30% CH_4 and 5 g $\text{Ni}/\text{Al}_2\text{O}_3\text{-SiO}_2$ catalyst. This KL had a longer fluent operation time than KL obtained from Sigma-Aldrich, which means the assumption that volatile and other compound contains carbon caused the agglomeration is true. Two pretreatment methods, torrefaction and pre-oxidation, were done for both lignin from Sigma-Aldrich and lignin from China. Both pretreatment methods can extend the time before blockage, among that pre-oxidation can allow both KL to be fluently fed into reactor in at least 40 min and nearly no blockage happened. Another agglomeration problem was found during formal lignin and CH_4 simultaneous pyrolysis experiments, When the effect of temperature on results was studied, although 600 °C had the highest oil yield, the temperature fluctuation caused by the reactions can make temperature increase to 620 °C, where agglomeration and blockage begin to happen, if temperature control (manually operated) was slow. Therefore, running experiments at 600 °C raised a high requirement on operation and agglomeration may also cause safety problem. Taking this into consideration, the optimal temperature condition for simultaneous pyrolysis experiments was chosen at 580 °C.

Table 5.2 Time before full blockage happened as a function of relevant operating conditions.

Run	Temperature (°C)	Pressure (bar)	Gas flow rate (L min ⁻¹)	Catalyst	Feedstock feeding rate (g min ⁻¹)	Feedstock	CH ₄ concentration (%)	Time before blockage happened
19	600	1	2	/	4.0	Pure Sigma lignin	0	27.5 s
20	600	1	2	/	1.3	Pure Sigma lignin	0	1 min 40 s
21	600	1	2	/	0.7	Pure Sigma lignin	0	2 min 25 s
22	600	1	2.2	/	0.7	Pure Sigma lignin	0	2 min 5 s
23	600	1	2.4	/	0.7	Pure Sigma lignin	0	1 min 48 s
24	600	1	1.8	/	0.7	Pure Sigma lignin	0	3 min 13 s
25	600	1	1.8	/	0.7	Sand:Sigma lignin=1:1	0	13 min 56 s
26	600	1	1.8	/	0.7	Sand:Sigma lignin=1.5:1	0	>40 min
27	600	1	1.8	/	0.7	Sand:Sigma lignin=1.5:1	4	33 min 38 s
28	600	1	1.8	/	0.7	Sand:Sigma lignin=1.5:1	30	>40 min
29	600	1	1.8	Ni/Al ₂ O ₃ - SiO ₂	0.7	Sand:Sigma lignin=1.5:1	0	3 min 41 s

Run	Temperature (°C)	Pressure (bar)	Gas flow rate (L min ⁻¹)	Catalyst	Feedstock feeding rate (g min ⁻¹)	Feedstock	CH ₄ concentration (%)	Time before blockage happened
30	600	1	1.8	Ni/Al ₂ O ₃ - SiO ₂	0.7	Sand:Sigma lignin=3:1	0	3 min 39 s
31	550	1	1.8	Ni/Al ₂ O ₃ - SiO ₂	0.7	Sand:Sigma lignin=3:1	0	4 min 17 s
32	500	1	1.8	Ni/Al ₂ O ₃ - SiO ₂	0.7	Sand:Sigma lignin=3:1	0	11 min 9 s
33	600	1	1.8	Ni/Al ₂ O ₃ - SiO ₂	0.7	Sand:CN lignin=3:1	0	19 min 1 s
34	600	1	1.8	Ni/Al ₂ O ₃ - SiO ₂	0.7	Sand: torrefaction Sigma lignin=3:1	30	23 min 4 s
35	600	1	1.8	Ni/Al ₂ O ₃ - SiO ₂	0.7	Sand: preoxidated Sigma lignin=3:1	30	>40 min
36	600	1	1.8	Ni/Al ₂ O ₃ - SiO ₂	0.7	Sand: preoxidated CN lignin=3:1	30	>40 min
37	600	1	1.8	Ni/Al ₂ O ₃ - SiO ₂	0.7	Sand: torrefaction CN lignin=3:1	30	31 min 13 s

5.4 Results and Discussion

This section discusses the impact of different operating parameters on the oil yield/GC-detectable oil yield in CH₄ and lignin simultaneous pyrolysis experiments. The GC-detectable oil will be called as light oil.

5.4.1 Effect of H₂ Source

In this section, a blank experiment without CH₄/H₂ and catalyst was done to compared with 3 experiments: inert experiment but with catalyst, 15.4% external H₂ with catalyst and 30% CH₄ with catalyst.

The product selectivity based on C in lignin conversion and lignin conversion is shown in Table 5.3. The deposit carbon generated by CH₄ under 580 °C and 1 bar the same CH₄ concentration atmosphere with 5 g Ni/Al₂O₃-SiO₂ catalyst was assumed to be constant, which was shown in Chapter 4. This assumption may cause error on results. Because the lignin pyrolysis can also generate CH₄ and BTEX, which can affect the process and result of DMA and CH₄ cracking. The gas selectivity was calculated by deducing oil and solid selectivity from 100%, because it is impossible to separate the CH₄ generated from lignin and CH₄ unreacted apart.

As is shown in Table 5.3, all four experiments had a low lignin conversion rate. That means many lignin did not have enough time to react in fluidized bed reactor. The high solid yield of these four experiments also proved that part of lignin was not fully reacted. Table 5.3 can also prove that the exist of catalyst and H₂ had an essential effect on the product distribution and lignin conversion rate. The 30% CH₄ experiment had a 10.3% higher lignin conversion than the no catalyst and no CH₄ experiment. Both oil and gas yield of 30% CH₄ experiment were significantly higher than no catalyst and no CH₄ experiment.

Table 5.3 Products yields and lignin conversion of different H₂ sources.

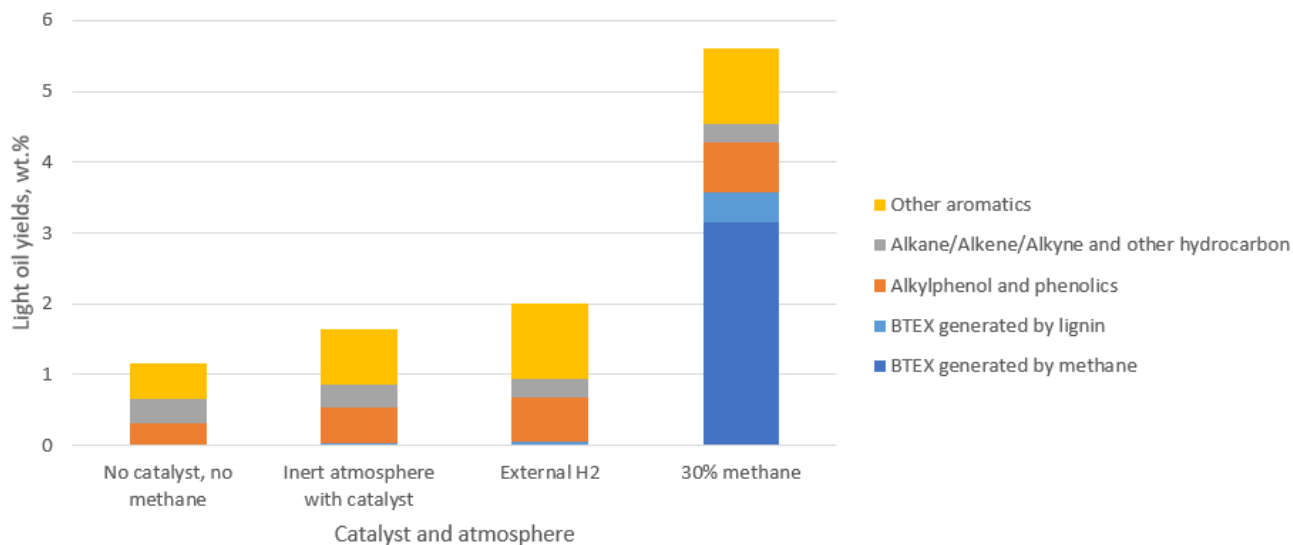
Catalyst and atmosphere	Solid, wt.%	Oil, wt.%	Gas, wt.%	Lignin Conversion, %
No catalyst, no CH ₄	68.5	17.1	14.4	62.2
Inert atmosphere, with catalyst	61.9	19.4	18.7	69.3
External H ₂	58.4	20.1	21.5	70.2
30% CH ₄	54.7	20.7	24.6	72.5

As is shown in Figure 5.1a, the blank lignin pyrolysis experiment without methane or catalyst had lowest light oil yields. When the Ni/Al₂O₃-SiO₂ catalyst was introduced in the system, yields increased for all light oil components. Especially alkylphenol and phenolics yield increased from 0.29 wt.% in blank experiment to 0.51 wt.% in inert atmosphere with catalyst experiment, and alkane/alkene/alkyne yield decreased from 0.35 wt.% in blank experiment to 0.31 wt.% in inert atmosphere with catalyst experiment. That means the Ni catalyst mainly aids the process of lignin crack into small molecules, however, the oxygen cannot be effectively removed.

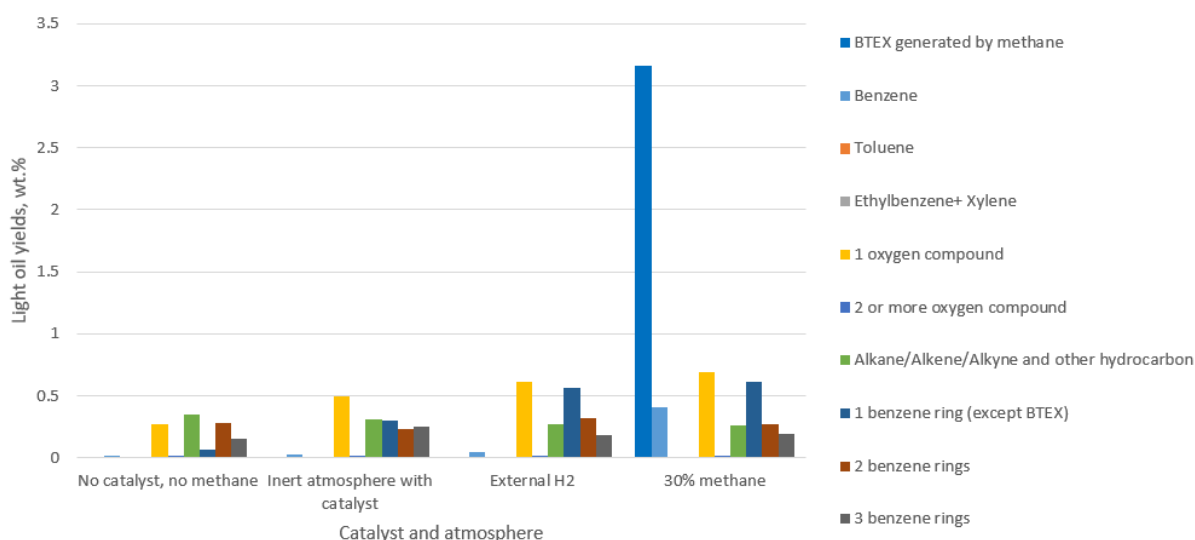
Figure 5.1a also compares the results between inert atmosphere with catalyst experiment and external H₂ experiment. The BTEX generated by lignin increased from 0.031 wt.% to 0.056 wt.% when 15.4% H₂ was introduced in system. Besides that, yield of other aromatics (which include all aromatics with one, two or three benzene rings and do not contains oxygen except BTEX) had an obvious increase from 0.79 wt.% to 1.1 wt.%, and Figure 5.1b showed that increase was because the yields of relatively small molecules increased (species with one benzene ring increased from 0.30 wt.% to 0.56 wt.% and those with two benzene rings from 0.24 wt.% to 0.32 wt.%). The yield of one-oxygen compounds in alkylphenol and phenolics also increased from 0.49 wt.% to 0.61 wt.%. These results showed that H₂ can help to break C-C, which allowed to obtain smaller molecules after pyrolysis than in experiments without H₂. The decrease in the alkane/alkene/alkyne (which may generate from benzene rings opening or short-chain alkane/alkene/alkyne polymerization) yield from 0.31 wt.% to 0.27 wt.% between

inert atmosphere with catalyst experiment and external H₂ experiment showed that H₂ will not break the structure of benzene ring (benzene ring opening may cause by temperature).^[128] The best yield result happened at 30% CH₄ experiment. The DMA reaction generated 3.2 wt.% BTEX which was the main increase in light oil yield. The in-situ generated H₂ also had a better performance than external H₂ in the conversion of KL to light oil. As is shown in Figure 5.1, in 30% CH₄ experiment, the BTEX generated by lignin has a significant increase to 0.21 wt.%, which mainly consisted of benzene. That means in-situ generated H₂ had a better performance in breaking C-C and C-O bond than external H₂. Thus, the in-situ H₂ generated by CH₄ was chosen as the optimal H₂ source in the following experiments. The data of external H₂ experiment and 30% CH₄ experiment described that the in-situ H₂ generated by CH₄ can be more effective picked by lignin and be involved in the lignin cracking process. The in-situ H₂ directly generated on the surface of catalyst, which is also the place that reaction happened most rapidly. That allows H₂ to have a better contact with reactants. When compared the result of light oil yield and total oil yield, the experiments with no H₂, both with catalyst and without catalyst, it can be observed that the lignin cannot be fully cracked which left many large compounds. That made these two experiments had highest fraction of oil contents outside the GC range.

Figure 5.1 shows that external H₂ can increase the light oil yield when compared with blank experiment, and the in-situ H₂ has an even better performance on Light oil yield increasing than external H₂. When compared with previous research,^[89] the light oil yield can very low (between 0.5 wt.% to 3.0 wt.%) if no CH₄ was injected into the reactor.



(a)



(b)

Figure 5.1 Light oil yields distribution during pre-oxidated Kraft lignin pyrolysis at 580 °C, 1bar, 3:1 sand:pre-treated lignin, Ni/Al₂O₃-SiO₂ catalyst, 2 L min⁻¹ flow rate, 1.5 g min⁻¹ feeding rate and different atmosphere conditions. (a). group, (b) more detailed disaggregation. The gas products result is shown in Table 5.4. The outlet CH₄ can come from two sources: unreacted inlet CH₄ and CH₄ generated by lignin, and it was impossible to separate these two sources apart.

The highest outlet H₂ concentration reached at external H₂ experiment. When compared with 30% CH₄ experiment which should generate equal amounts of H₂ with 15.4% external H₂

experiment, less H₂ was picked by KL in external H₂ experiment and that made it have higher outlet H₂ concentration. The 30% CH₄ experiment achieved the highest CO and CO₂ concentrations. These oxygens were from oxhydryl in lignin monomer and C-O bond between two lignin monomers. This high CO and CO₂ concentration showed H₂ generated by CH₄ can be efficiently picked by lignin.

Table 5.4 Outlet gas composition in H₂ source experiments. (N₂ as background gas)

	No catalyst and CH ₄ (vol.%)	Inert atmosphere with catalyst (vol.%)	External H ₂ (vol.%)	30% CH ₄ (vol.%)
H ₂	0.3	0.4	11.1	9.3
CO	6.4	8.9	9.2	10.2
CO ₂	0.4	0.3	0.5	1.1
CH ₄	0.7	1.0	0.9	19.8

5.4.2 Effect of Temperature

In this section, four experiments under 560 °C, 580 °C, 600 °C and 620 °C were done to test the influence of temperature on the result of KL and CH₄ simultaneous pyrolysis. That was based on the result from Chapter 4 that the optimal temperature for CH₄ to generate H₂ happened within the range of 550 °C to 650 °C. The result of this section can also help to determine if the pyrolysis result was stable when temperature slightly changed.

The lignin conversion rate first increased from 71.4% in 560 °C to 76.1% in 600 °C, and then decreased to 72.6% in 620 °C. (shown in Table 5.5) That was caused by the deactivation of catalyst for the catalyst agglomeration which has been illustrated above. The carbon generated by CH₄ and lignin can further speed up the catalyst agglomeration (the solid yield was higher in 620 °C than in 600 °C, this additional solid should be the carbon generated by lignin cracking under higher pressure). Not like the result of light oil yield, the total oil yield of 620 °C experiment was higher than the result in 560 °C and 580 °C. That means the higher temperature and pressure help to crack more lignin into liquid phase compounds. However, this cracking

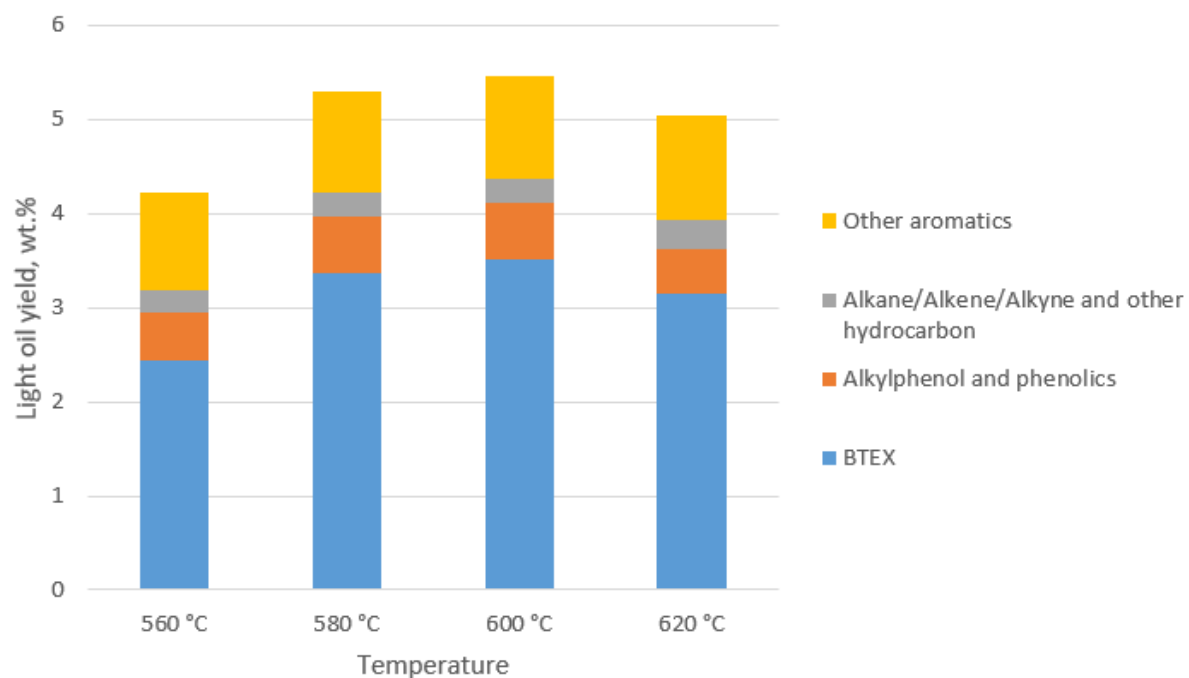
was not enough and many of these liquid phase compounds were still too heavy for GC detector. The total gas yield was in an increasing trend before 600 °C (the gas yield in 580 °C and 600 °C was similar which can be considered as an experimental error), and that was because higher temperature tends to crack more lignin. However, under 620 °C, the pressurize in reactor can inhibit the generation of H₂ from CH₄, which caused the reduction of gas yield.

Table 5.5 Products yields and lignin conversion of different Temperature.

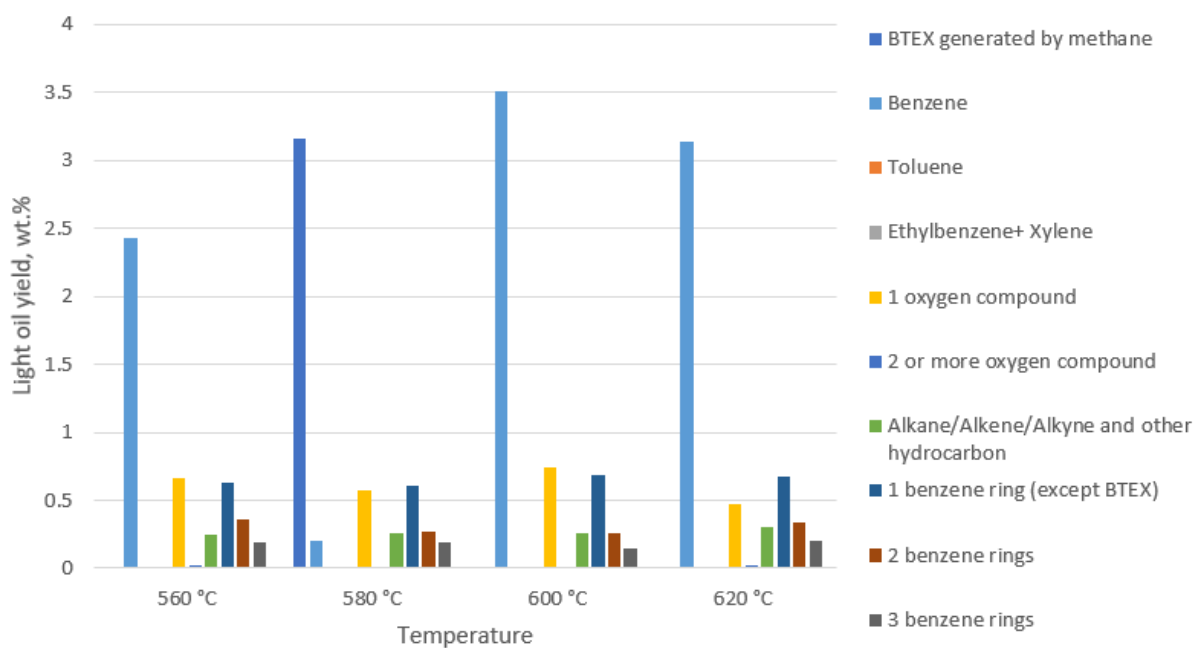
Temperature, °C	Solid, wt.%	Oil, wt.%	Gas, wt.%	Lignin Conversion, %
560	57.2	20.3	22.5	71.4
580	54.7	20.7	24.6	72.5
600	51.9	23.6	24.5	76.1
620	55.5	21.4	23.1	72.6

Figure 5.2 shows that the best light oil yield happened at 600 °C. At that temperature, both yield of BTEX (3.52 wt.%) and compounds with one oxygen (0.68 wt.%) were at the highest level within these series of experiments. At temperatures lower than 600 °C, the light oil yield kept a raising trend with temperature, mainly because the yield of benzene generated by CH₄ increased. However, at 620 °C, agglomeration began to happen and caused the pressure in the reactor to increase. This pressure increase had a negative effect on the yield of benzene generated in DMA reaction. Although higher pressure allows more H₂ to be picked by lignin and generate more benzene, the result showed that under 620 °C experiment condition, the decrease on benzene generated by DMA was more significant when compared with the increase on benzene generated by lignin. The agglomeration between catalyst and sand or lignin can also accelerate the deactivation of catalyst. In that case, even if lignin and CH₄ were still able to enter the reactor, the condition was not suitable for CH₄ and lignin simultaneous pyrolysis reactions.

As is shown in Figure 5.2b, the toluene, ethylbenzene and xylene yield were very low. That shows the lignin was not fully cracked. It still had many large molecules exist and needed to be cracked.



(a)



(b)

Figure 5.2 Light oil yields distribution during pre-oxidated Kraft lignin pyrolysis at 1bar, 30% methane, 3:1 sand:pre-treated lignin, Ni/Al₂O₃-SiO₂ catalyst, 2 L min⁻¹ flow rate, 1.5 g min⁻¹ feeding rate and different temperature. (a). group, (b) more detailed disaggregation.

The gas product composition is shown in Table 5.6. According to the result in Section 4.3.3, the H₂ generated by DMA should reach its highest level at 600 °C. However, in the outlet gas, the 600 °C experiment had the lowest H₂ concentration, probably reflecting that at this temperature H₂ reaction with lignin was enhanced.

Table 5.6 Outlet gas composition in temperature experiments. (N₂ background gas)

	560 °C (vol.%)	580 °C (vol.%)	600 °C (vol.%)	620 °C (vol.%)
H ₂	8.7	9.3	7.2	8.2
CO	9.6	10.2	10.8	10.1
CO ₂	0.7	1.1	1.2	2.1
CH ₄	19.9	19.8	21.2	19.0

5.4.3 Effect of Feeding Rate

The influence of total feeding rate of sand and KL mixture to the pyrolysis experiments result was discussed in this section. Four different feeding rate experiments, 0.7 g min⁻¹ (which is the minimum feeding rate for feeding motor stably working), 1.5 g min⁻¹, 2.0 g min⁻¹ and 2.5 g min⁻¹, were done.

The lignin conversion rate of the 0.7 and 1.5 g min⁻¹ experiments did not have obvious difference. But when feeding rate continued to increase from 1.5 g min⁻¹ to 2 and 2.5 g min⁻¹, the lignin conversion showed a decreasing trend (shows in Table 5.7). That was because, as discussed above, at 580 °C and 2 L min⁻¹ only limited lignin can be reacted in time in reactor. Higher feeding rate means that even more lignin, which amount exceeded the highest amount that can be reacted in time, were fed into reactor. The overfed part of lignin might have an even lower conversion rate. This decreasing trend from 1.5 g min⁻¹ to 2.5 g min⁻¹ can also be observed in total oil + gas yield. That shows the reacted lignin cannot be fully cracked under higher feeding rate to generate small molecules oil and gas.

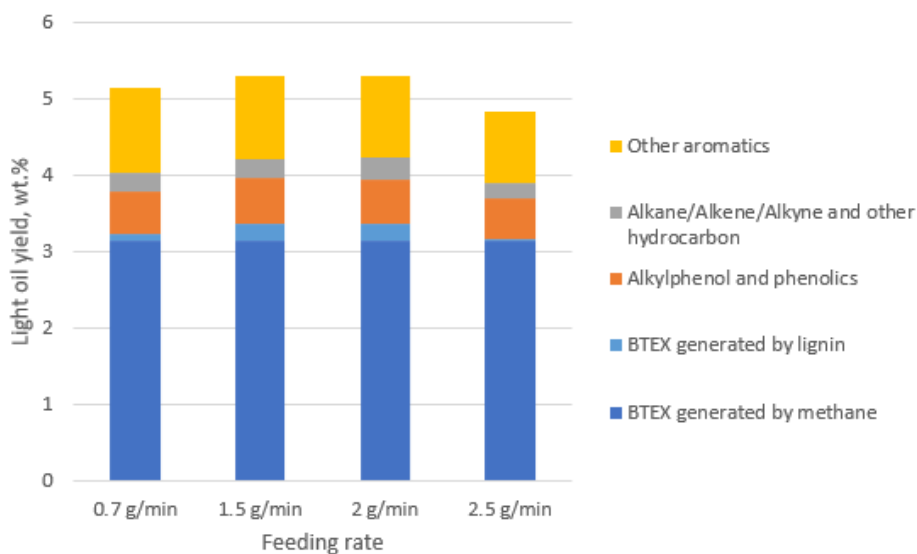
Table 5.7 Products yields and lignin conversion of different feeding rate.

Feeding rate, g min ⁻¹	Solid, wt.%	Oil, wt.%	Gas, wt.%	Lignin Conversion, %
0.7	56.1	20.4	23.5	72.3
1.5	54.7	20.7	24.6	72.5
2	55.6	20.8	23.6	71.5
2.5	57.3	19.6	23.1	70.3

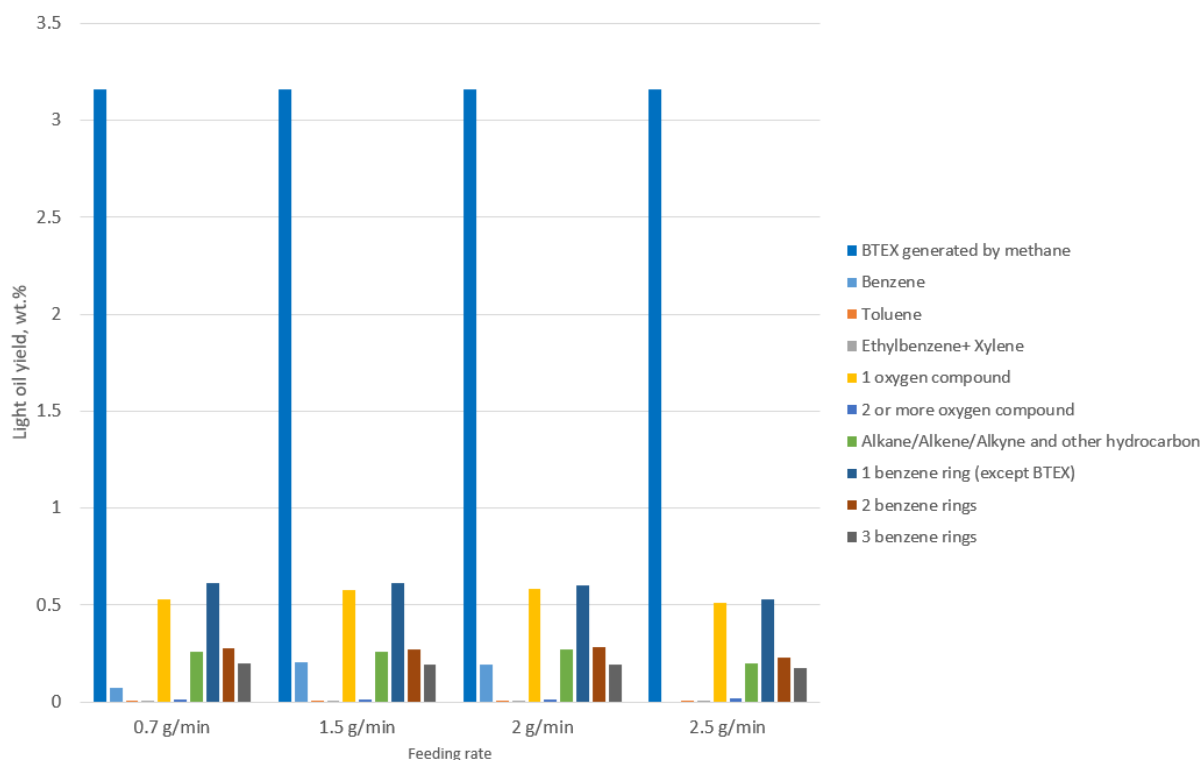
Figure 5.3 shows that feeding rate did not have an obvious influence on the total yield and BTEX yield. The best performance was obtained at 1.5 g min⁻¹, which had a 5.3 wt.% total yield and 3.4 wt.% BTEX yield (0.21 wt.% generated by lignin). The total light oil yield of 2.0 g min⁻¹ experiment was very close to the best one. In 2.0 g min⁻¹ experiment, the total light oil yield was 5.3 wt.% and the BTEX generated by lignin yield, which was 0.20 wt.%, was slightly lower than the 1.5 g min⁻¹ experiment. However, when the total feedstock weight was not changed, the 2.0 g min⁻¹ experiment would end in a shorter time than the 1.5 g min⁻¹ one. That made 2.0 g min⁻¹ experiment had a shorter time in steady state which might cause larger error. Thus, the optimal condition was chosen at 1.5 g min⁻¹.

A major decrease of total light oil yield happened at 2.5 g min⁻¹. That was because when the feeding rate was too high, a large amount of incompletely reacted heavy oil generated by lignin could adhere to the surface of solid materials (bed material, catalyst or unreacted lignin) and made these solid materials easy to sticked with each other and generate large particle size material. This large particle size material could deposit on the bottom of reactor and did not have time to be carried up. That made blockage happened. Even if this blockage did not stop the feeding, it can still reduce the total light oil yield. As shown in Figure 5.3b, if assuming the yield of BTEX yield generated by CH₄ in 2.5 g min⁻¹ equals to that obtained with CH₄ in the absence of lignin, which has been illustrated in section 5.4.1, no BTEX would have come from lignin pyrolysis, which is contradictory with the fact that lignin pyrolysis did generate other compounds. Thus, the BTEX generated by CH₄ must be lower than other feeding rate and the error came from the assumption cannot be ignored. It is likely that the pressurization caused by

a minor blockage was behind this effect.



(a)



(b)

Figure 5.3 Light oil yields distribution during pre-oxidated Kraft lignin pyrolysis at 580 °C, 1bar, 30% methane, 3:1 sand:pre-treated lignin, 5g Ni/Al₂O₃-SiO₂ catalyst, 2 L min⁻¹ flow rate and different feeding rate. (a). group, (b) more detailed disaggregation.

The gas result did not have important difference between 0.7 g min⁻¹, 1.5 g min⁻¹ and 2 g min⁻¹

¹ experiments (shown in Table 5.8). Generally, the feeding rate did not have obvious influence on gas products. But because the pressure had an increase in reactor, the H₂ generated by methane decreased in 2.5 g min⁻¹ experiment. In this feeding rate, the concentration of CO decreased and the concentration of CO₂ increased. That was because higher pressure profited H₂ to be picked by C-O bonds in KL and removed more oxygen from KL.

Table 5.8 Outlet gas composition in feeding rate experiments. (N₂ background gas)

	0.7 g min ⁻¹ (vol.%)	1.5 g min ⁻¹ (vol.%)	2 g min ⁻¹ (vol.%)	2.5 g min ⁻¹ (vol.%)
H ₂	9.6	9.3	9.0	8.1
CO	9.4	10.2	9.9	8.8
CO ₂	0.9	1.1	1.3	2.1
CH ₄	20.1	19.8	19.7	20.4

5.4.4 Effect of Catalyst Amount

As shown in Section 4.3.2, 1.56 g was not a suitable amount for catalyst in this set up. At that condition, the unavoidable weight loss of catalyst during the experiment caused by carrier gas cannot be considered negligible, and the carrier gas flow rate cannot be reduced too much because the total gas flow rate under room temperature should higher than the terminal velocity of sand mixed with lignin in spout line. Thus, for the study of simultaneous DMA and lignin depolymerization reactions 3.5 g of catalyst was set as the low-level catalyst amount to test the effect of this parameter against 5 g of catalyst as employed in Chapter 4.

Not like the low-level (1.56 g) catalyst amount experiment result in Chapter 4, 3.5 g low level Ni/Al₂O₃-SiO₂ catalyst can well catalyst both DMA reaction and lignin pyrolysis. The lignin conversion rate and oil yield of 3.5 g catalyst experiment were only slightly lower than 5 g catalyst experiment, which can be obtained from Table 5.9. However, the 5 g catalyst experiment had higher gas yield than 3.5 g catalyst one. That was because more catalyst in reactor can promote DMA reaction to generate more H₂ than less catalyst amount. This additional H₂ can further join in lignin cracking and remove more oxygen from lignin. Then, this removed oxygen can generate CO and CO₂ which further increased the gas yield.

Table 5.9 Products yields and lignin conversion of different catalyst amount.

Catalyst amount, g	Solid, wt.%	Oil, wt.%	Gas, wt.%	Lignin Conversion, %
3.5	59.3	19.9	20.8	71.1
5	54.7	20.7	24.6	72.5

The results shown in Figure 5.4 reflect that more catalyst led to higher light oil yield. The total light oil yield for the 3.5 g catalyst experiment was 4.2 wt.% and this number for 5 g catalyst experiment was 5.3 wt.%. Different with the result discussed in Chapter 4, the 3.5 g catalyst had a similar light oil yield/catalyst weight ratio with 5 g catalyst. That means in 3.5 g catalyst experiment the catalyst by-pass problem (discussed in Chapter 4) did not play a significant role in product generation.

Figure 5.4(b) shows some interesting results in terms of the oil composition. Although the total yield was lower than 5 g catalyst experiment, the 3.5 g had a higher yield of compounds with three benzene rings, which was 0.49 wt.% vs. 0.19 wt.% for the 5 g catalyst experiment. On the other hand, the experiment carried out with 5 g of catalyst led to a much higher yield of compounds with one benzene ring, 0.61 wt.% vs. 0.08 wt. %. The gas concentration results in Table 5.10 also show that 5 g catalyst can generate more CO and CO₂ (10.2 vol.% and 1.1 vol.% in 5g catalyst experiment vs 7.3 vol.% and 0.5 vol.%), which are the by-products of lignin pyrolysis. All these results showed the advantage of using more catalyst to fully crack lignin and its derivatives to generate target products BTEX. Further increase the amount of catalyst may improve the product distribution and light oil yield, but more catalyst means higher economic costs, and the bed length and fluidizing condition can be changed if the catalyst amount is much higher than 5 g.

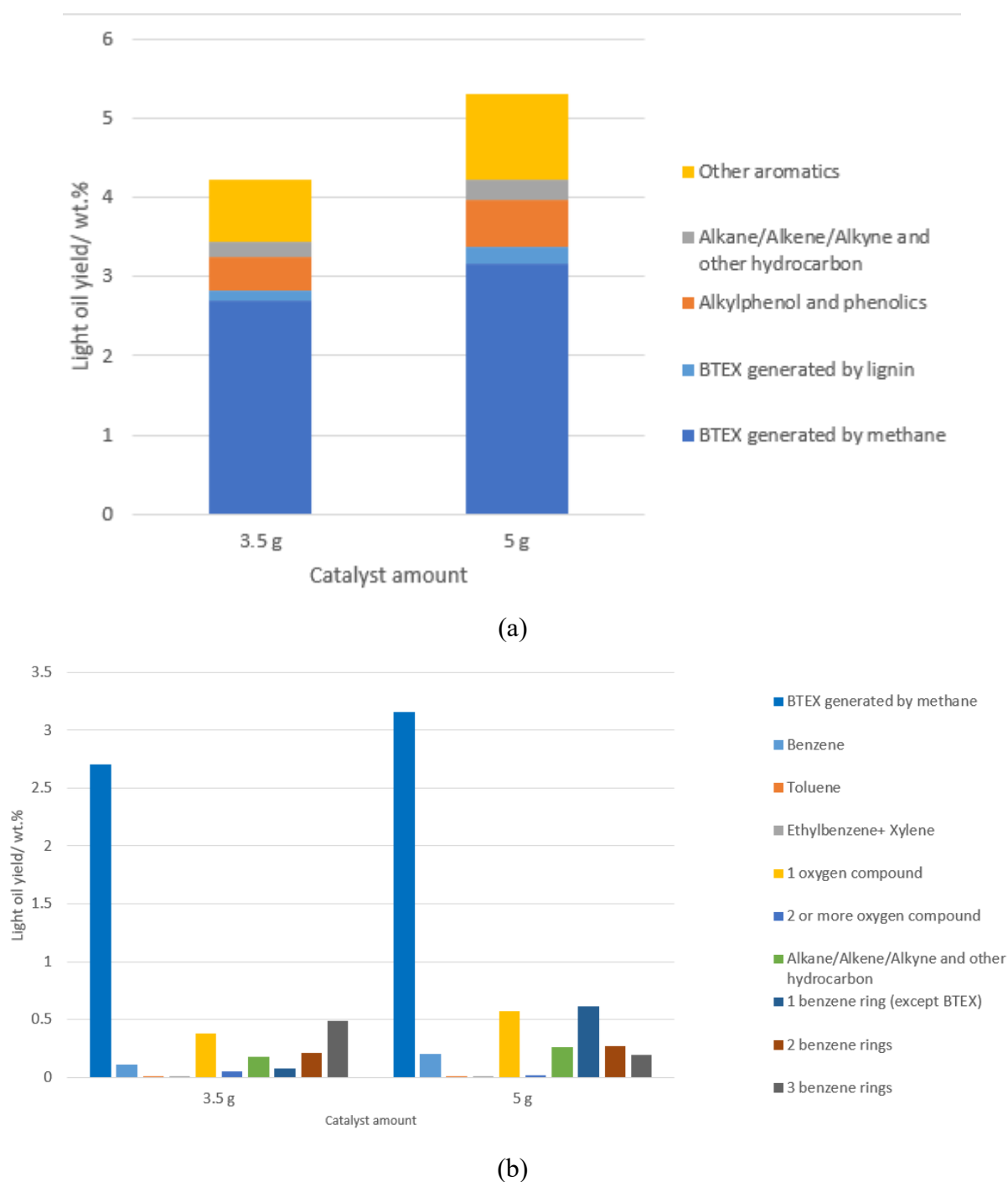


Figure 5.4 Light oil yields distribution during pre-oxidated Kraft lignin pyrolysis at 580 °C, 1bar, 30% methane, 3:1 sand:pre-treated lignin, Ni/Al₂O₃-SiO₂ catalyst, 2 L min⁻¹ flow rate, 1.5 g min⁻¹ feeding rate and different catalyst amount. (a). group, (b) more detailed disaggregation.

Table 5.10 Outlet gas composition in catalyst amount experiments. (N₂ background gas)

	3.5 g (vol.%)	5 g (vol.%)
H ₂	7.5	9.3
CO	7.3	10.2
CO ₂	0.5	1.1
CH ₄	22.5	19.8

5.4.5 Effect of Gas Flow Rate

Three experiments were done to test the influence of gas flow rate to product yield. The gas flow rate first reduced from highest 2 L min⁻¹ to a mid-level 1.6 L min⁻¹, and then to the lowest 1.15 L min⁻¹ which is the minimum gas flow rate required to allow the sand mixed with KL to be carried into the reactor.

The decrease of gas flow rate significantly increased the lignin conversion rate. This proved that in previous experiment conditions, the part of lignin and volatiles did not have enough time to stay in reactor for reaction. Some small particle size lignin can be carried by gas and flow out from the reactor under high gas flow rate. Under 1.15 L min⁻¹ (which is the lowest gas flow rate to allow dilution sand to be carried and flows into reactor), the lignin conversion rate was 12.9% higher than the result in 2 L min⁻¹ (illustrates in Table 5.11). This essential improvement can also be obtained in total oil yield and gas yield, as the longer residence time allows not only more unreacted lignin to be cracked into oil, but also some volatile to be further cracked into CO and CO₂.

Table 5.11 Products yields and lignin conversion of different gas flow rate.

Gas flow rate, L min ⁻¹	Solid, wt.%	Oil, wt.%	Gas, wt.%	Lignin Conversion, %
2	54.7	20.7	24.6	72.5
1.6	50.3	24.9	24.8	79.5
1.15	48.5	26.2	25.3	85.4

An obvious improvement on total light oil yield happened when decreasing the gas flow rate from 2 L min⁻¹ to 1.6 and 1.15 L min⁻¹. That showed some lignin and volatile by-passed the

reactor under high total feed gas flow rate condition. As is mentioned in Chapter 3, the reason why using high total feed gas flow rate at first was because the feeding gas should meet the requirement of carry the sand (particle size less than 150 μm) mixed with lignin up into the reactor, which has been illustrated in Chapter 3.

As is shown in Figure 5.5a, the highest total yield was 9.97% which was gotten at 1.15 L min⁻¹ total feed gas flow rate. This number was obviously higher than the result from the 1.6 L min⁻¹ experiment, which had a 7.1 wt.% total light oil yield. All yields of BTEX generated by lignin, alkylphenol and phenolics and other aromatics in 1.15 L min⁻¹ were higher than at 1.6 L min⁻¹. This proved that more lignin reacted in the 1.15 L min⁻¹ experiment, which reached an alkylphenol and phenolics yield of 2.7 wt.%, significantly higher than the BTEX yield generated by lignin (1.8 wt.%) and other aromatics (2.1 wt.%). Although the yields of all products increased when gas flow rate reduced, the yield of alkylphenol and phenolics still had the highest increase and becomes major product under more lignin and volatile reacted 1.15 L min⁻¹ experiment. This result shows that Ni/Al₂O₃-SiO₂ catalyst cannot ideally removed the oxygen on the oxhydryl and the link of two lignin monomer. This can be also proved by the data shown in Figure 5.5b. In Figure 5.5b, the compounds which had the highest yield were those containing one oxygen (2.5 wt.%). Based on the structure of lignin monomer given by Sigma-Aldrich, which was shown in Chapter 3, these mono-oxygenated compounds were left after the C-C bond between two lignin monomers was broken. The oil after the 1.15 L min⁻¹ experiment still contained many large molecules (0.51 wt.% with two benzene rings and 0.22 wt.% with three benzene rings) which would need to be further pyrolysed. Another thing needs to be discussed here was under 1.15 L min⁻¹ total feed gas flow rate, the yield of long chain alkane/alkene/alkyne and other hydrocarbon, which was 0.14 wt.%, was lower than the yield of them under 1.6 L min⁻¹ (0.27 wt.%) and 2 L min⁻¹ (0.26 wt.%). That showed the catalyst which can break C-C bond, and can also restrained the re-polymerization.

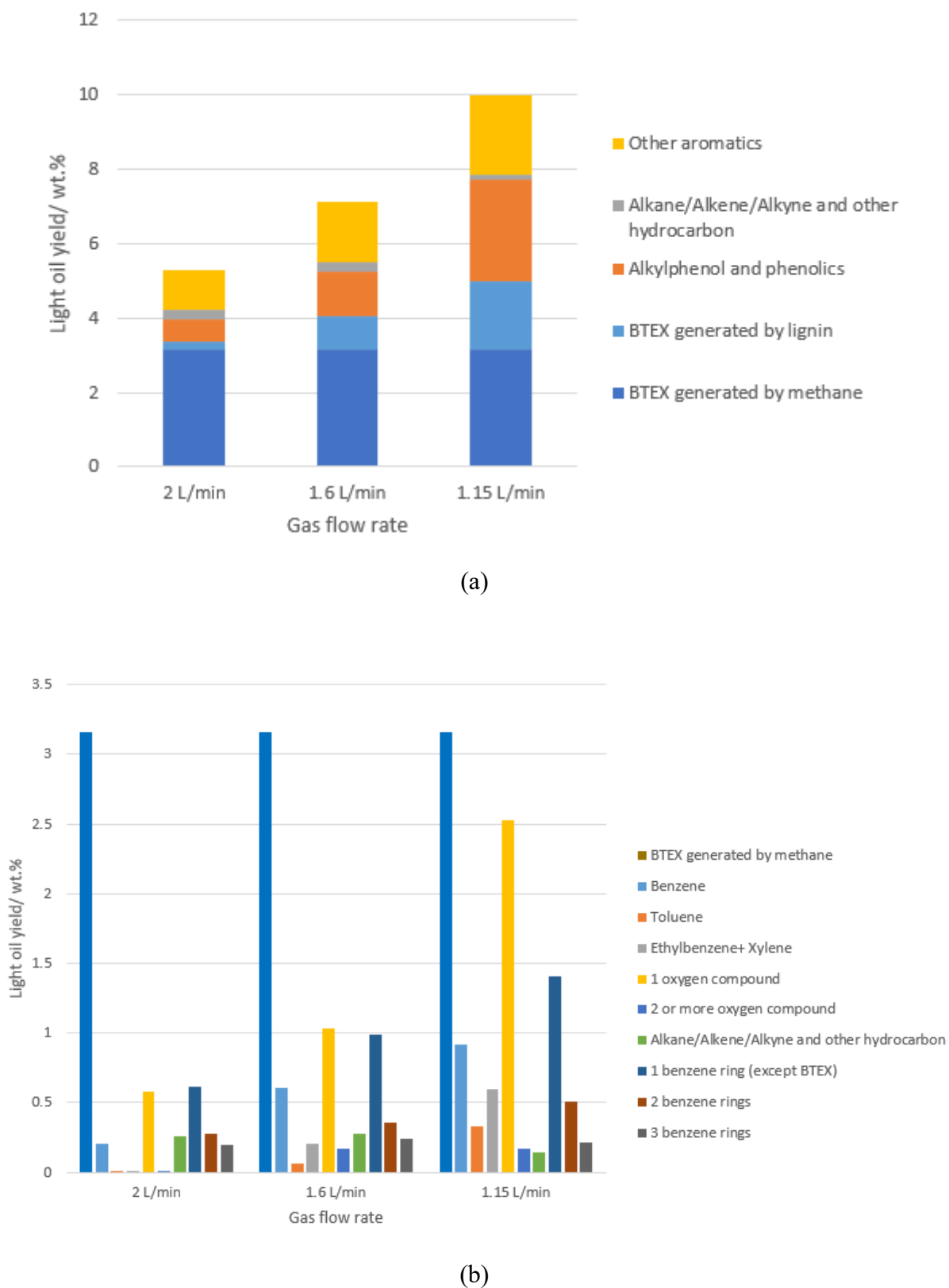


Figure 5.5 Light oil yields distribution during pre-oxidated Kraft lignin pyrolysis at 580 °C, 1bar, 30% methane, 3:1 sand:pre-treated lignin, 5g Ni/Al₂O₃-SiO₂ catalyst, 1.5 g min⁻¹ feeding rate and different total feed gas flow rate. (a). group, (b) more detailed disaggregation.

If assume under the same temperature, pressure and CH₄ concentration, the H₂ generated from DMA reaction was the same, the result in Table 5.12 can prove that more H₂ was consumed in lignin pyrolysis for longer residence time caused by lower gas flow rate. This longer residence time also allowed more lignin to be cracked and generate CO and CO₂ (both of which had the highest concentration at 1.15 L min⁻¹ experiment). These results also proved the residence time had a major influence for gas concentration generated by lignin in this fluidized bed system.

Table 5.12 Outlet gas composition in catalyst amount experiments. (N₂ background gas)

	2 L min ⁻¹ (vol.%)	1.6 L min ⁻¹ (vol.%)	1.15 L min ⁻¹ (vol.%)
H ₂	9.3	5.8	3.4
CO	10.2	11.5	13.8
CO ₂	1.1	2.3	3.1
CH ₄	19.8	21.3	22.1

5.4.6 Effect of Feedstock Dilution Ratio

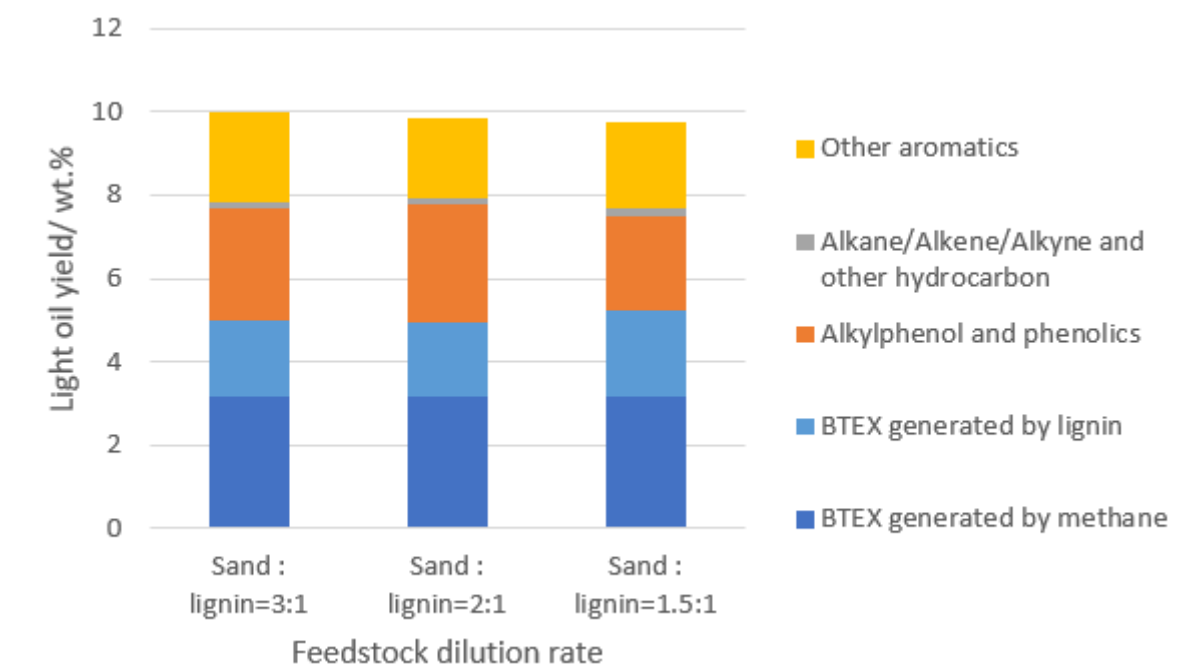
Three dilution rate of sand and lignin experiments were run in this section. The sand to lignin ratio decreased from 3:1 to 2:1 and 1.5:1.

It is the same with the light oil yield. The lignin conversion rate was not much affected by feedstock dilution rate. As is described in Table 5.13, the total oil yield was only slightly lower in 1.5:1 ratio experiment than in two others. That made choosing 1.5:1 as the sand and lignin mixture ratio become an ideal choice to avoid using too much small particle size sand, which is expensive.

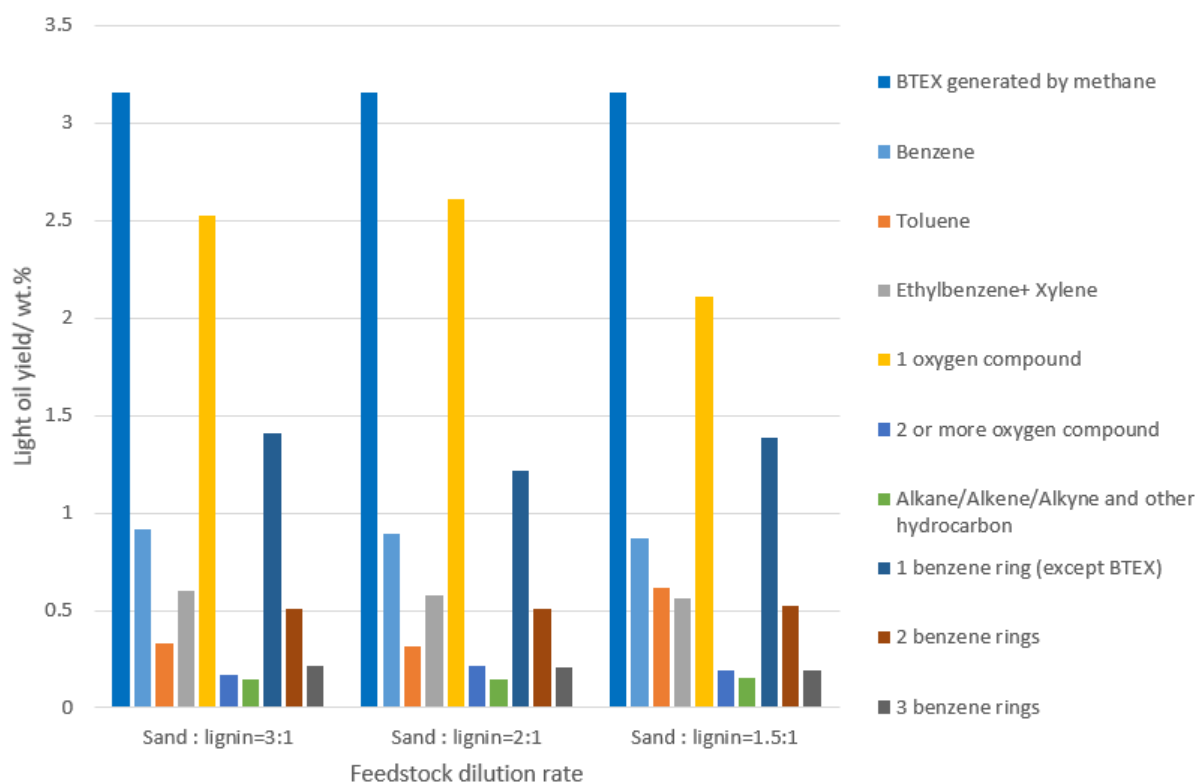
Table 5.13 Products yields and lignin conversion of different feedstock dilution rate.

Feedstock dilution rate, sand : lignin	Solid, wt.%	Oil, wt.%	Gas, wt.%	Lignin Conversion, %
3:1	48.5	26.2	25.3	85.4
2:1	48.8	26.1	25.1	85.3
1.5:1	48.3	25.9	25.8	85.7

As shown in Figure 5.6a, the dilution ratio did not have an obvious influence on total light oil yield. When the sand : lignin ratio was reduced, the total light oil yield showed a decreasing trend. This trend was mainly caused by the decrease in alkylphenol and phenolics (specifically, mono-oxygenated compounds, as shown in Figure 5.6(b)). An interesting change shown in Figure 5.6b that although the total light oil yield of sand : lignin = 1.5:1 experiment was lowest (9.8 wt.%), the yields of toluene (0.62 wt.%), ethylbenzene, xylene (ethylbenzene + xylene yields 1.2 wt.%) and 1 benzene ring aromatics (1.37 wt.%) were obviously higher than the yields in the other two experiments. The decrease of mono-oxygenated aromatics was partly due to the oxygen being further removed from the benzene ring. The results on outlet gas concentration in Table 5.14 also proved that. Because in these experiments, the lignin was the only oxygen source. The oxygen in product gases CO and CO₂ must come from lignin. The high concentration of CO and CO₂ in 1.5:1 experiment showed this condition can help to remove the oxygen from benzene rings. Thus sand:lignin = 1.5:1 can produce more target products and it was chosen as the optimal condition in following experiments. The yield of total BTEX generated by lignin in the 1.5:1 experiment was 2.05 wt.% which was also higher than 1.84 wt.% in 3:1 experiment and 1.79 wt.% in 2:1 experiment. That is because at the same feeding rate, 1.5:1 experiment fed more lignin into reactor at the same time. As was discussed in Section 5.4.3, this higher amount of lignin fed into reactor might increase the pressure in the reactor, which can improve the efficiency of H₂ picked by lignin and C-O bond.



(a)



(b)

Figure 5.6 Light oil yields distribution during pre-oxidated Kraft lignin pyrolysis at 580 °C, 1bar, 30% methane, 5g Ni/Al₂O₃-SiO₂ catalyst, 1.15 L min⁻¹ flow rate, 1.5 g min⁻¹ feeding rate. (a). group, (b) more detailed disaggregation.

The gas products result is shown in Table 5.14. The increase of CO₂ concentration in 1.5:1

experiment was caused by pressurizing in reactor, which allowed that more oxygen can be cracked from lignin. The gas results only had limited differences between 3:1, 2:1 and 1.5:1 experiments, which matched with the total gas yield result. That means the change of feedstock dilution ratio from 3:1 to 1.5:1 was acceptable in following experiments.

Table 5.14 Outlet gas composition in feedstock dilution ratio experiments. (N₂ background gas)

	Sand : lignin=3:1 (vol.%)	Sand : lignin=2:1 (vol.%)	Sand : lignin=1.5:1 (vol.%)
H ₂	3.4	3.3	2.7
CO	13.8	13.4	13.9
CO ₂	3.1	2.8	3.7
CH ₄	22.1	22.6	22.8

5.4.7 Effect of Pressure

Pressure effect experiments were done at 1 bar, 3 bar and 5 bar. High pressure can reduce the H₂ and oil yields from DMA reaction, according to thermodynamic equilibrium principle. But high pressure can also promote the light oil yields from lignin pyrolysis. The water (generated by lignin and cannot be detected by GC) and gas shift may also happen under higher temperature. And because the water generated in reactor cannot be detected by both on-line gas analyzer and GC, higher water concentration can importantly affect the mass balance of experiment. Thus, a balance needs to be found between these two processes which can reach a high oil yield. That is why an even higher pressure was not chosen in these experiments.

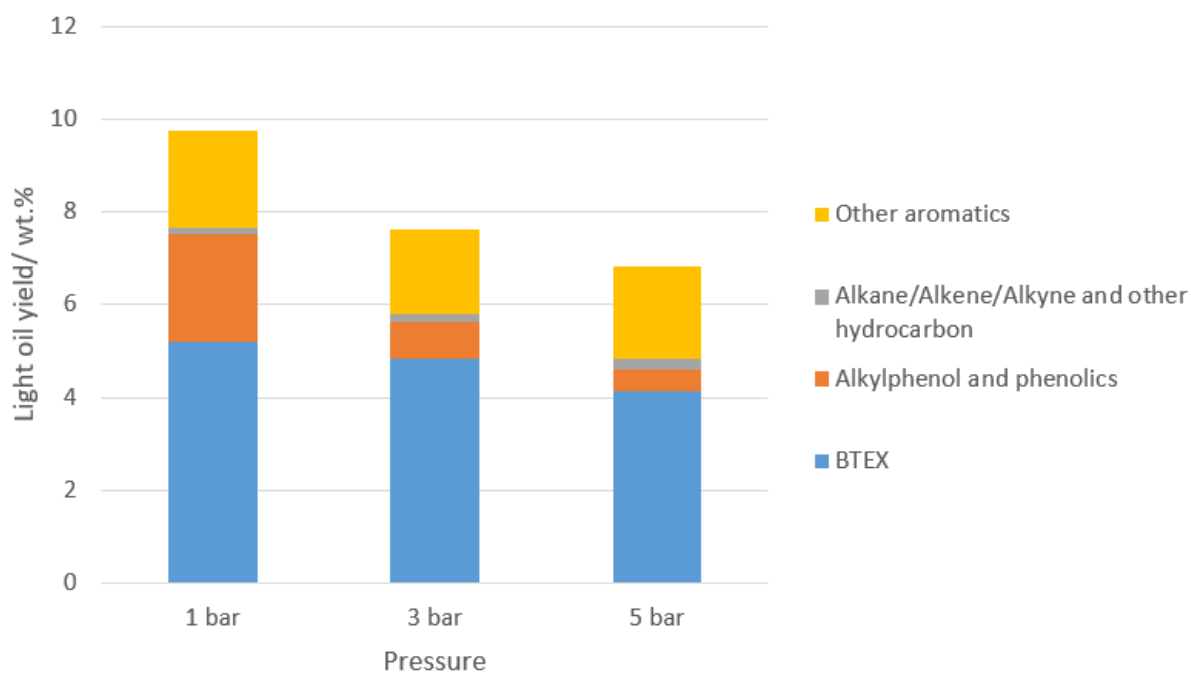
According to the result obtained from Table 5.15, not like the results in light oil yield, the lignin conversion rate was increased when pressure increasing. That was because, although the H₂ generated by CH₄ decreased, the H₂ can more efficiently participate in lignin pyrolysis under high pressure experiments. The influence of H₂ concentration decrease on lignin cracking was less than the effect of H₂ utilization coefficient increase. However, when taking CH₄ into account, the total oil yield decreased when pressure increased. That was because as one of the major oil products, the oil from CH₄ significantly decreased. The gas yield first decreased from 25.8 wt.% in 1 bar experiment to 23.7 wt.% in 3 bar experiment, (which was caused by the

CH₄ generated H₂ yield decreased) and then increased to 24.9 wt.% in 5 bar experiment (which was because essential increase on the CO and CO₂ generation).

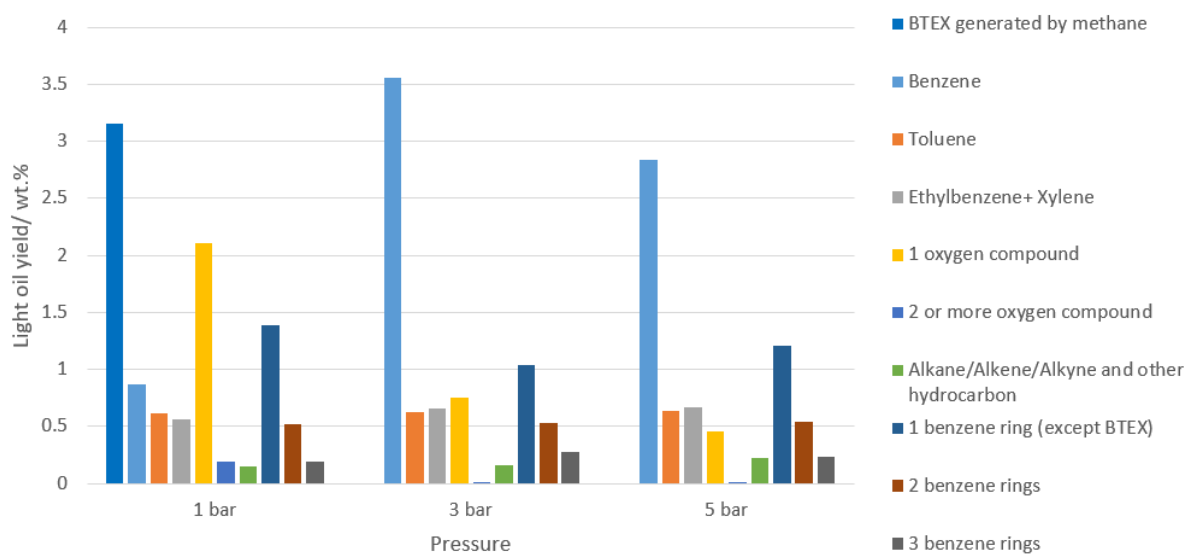
Table 5.15 Products yields and lignin conversion of different pressure.

Pressure, bar	Solid, wt.%	Oil, wt.%	Gas, wt.%	Lignin Conversion, %
1	48.3	25.9	25.8	85.7
3	51.1	25.2	23.7	86.4
5	50.1	25.0	24.9	88.3

Figure 5.7a showed that the pressure rising can significantly reduce the total yield (9.8 wt.% in 1 bar, 7.6 wt.% in 3 bar, 6.8 wt.% in 5 bar). That was because the high pressure can inhibit DMA to happen due to thermodynamic equilibrium. That means the yields of H₂ and BTEX from CH₄ decrease when pressure raises. However, the BTEX yields at different pressures did not have large differences (Figure 5.7a). They were 5.21 wt.% at 1bar, 4.85 wt.% at 3 bar, and 4.15 wt.% at 5 bar. This may be due to the enhancement of hydrodeoxygenation reactions of the aromatic rings at higher pressure. That can be proved by the data shown in Figure 5.7a and 5.7b, the alkylphenol and phenolics yield (2.3 wt.% in 1 bar, 0.77 wt.% in 3 bar, 0.46 wt.% in 5 bar) and two or more oxygen compounds (0.19 wt.% in 1 bar, and lower than 0.01 wt.% in 3 and 5 bar) had a significant decrease when pressure increased. For the yield of one oxygen compound, it firstly increased from 2.11 wt.% in 1 bar to highest 7.57 wt.% in 3 bar, and then decreased to 4.57 wt.% in 5 bar. That was because during pressure raising two or more oxygen compounds were firstly converted into one oxygen compound, and when the pressure continued raising, the oxygen was further removed from one oxygen compounds. The benzene rings which had oxygen removed then continued being pyrolyzed into smaller molecules. That made the yields of ETX and compounds with one benzene ring increase, as shown in Figure 5.7b. The reduced superficial velocity at high pressure allowed the volatile and intermediate solid products (which had smaller particle size) from lignin pyrolysis to have longer residence time and react more completely.



(a)



(b)

Figure 5.7 Light oil yields distribution during pre-oxidated Kraft lignin pyrolysis at 580 °C, 1.5:1 sand:pre-treated lignin, 30% methane, 5g Ni/Al₂O₃-SiO₂ catalyst, 1.15 L min⁻¹ flow rate, 1.5 g min⁻¹ feeding rate. (a). group, (b) more detailed disaggregation.

The gas product results are shown in Table 5.16. The result showed that high pressure can obviously increase the concentration of CO and CO₂. That is another evidence which proves high pressure can help to remove oxygen from lignin. The significantly decreased H₂ concentration was not only because more H₂ was consumed during breaking C-O bond, but the

amount H₂ generated by DMA reaction was also reduced. That matched the conclusion gotten from Figure 5.7.

Table 5.16 Outlet gas composition in pressure experiments. (N₂ background gas)

	1 bar (vol.%)	3 bar (vol.%)	5 bar (vol.%)
H ₂	2.7	1.3	0.3
CO	13.9	16.5	19.1
CO ₂	3.3	7.1	9.9
CH ₄	22.8	16.7	15.1

5.4.8 Effect of CH₄ Concentration

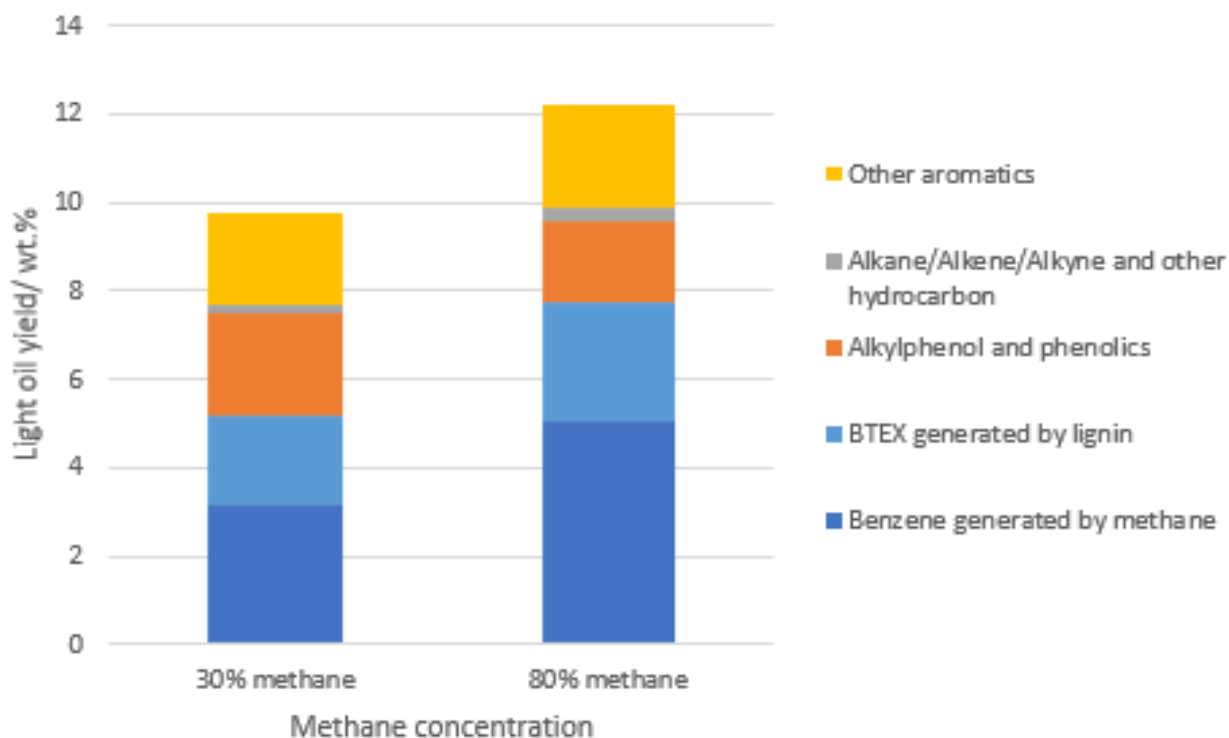
Based on the discussion in Chapter 4, the 80% CH₄ was used as the high level to compare with the 30% CH₄ low level and test the influence of CH₄ concentration. The atmosphere which had a better performance on oil generation would be used as the set point in catalyst experiments in Chapter 4.

As is shown in Table 5.17, the 80% CH₄ concentration in inlet gas experiment reached a similar lignin conversion rate with 3 bar and 30% CH₄ concentration experiment (illustrated in Section 5.4.7). That was because higher CH₄ concentration can generate more H₂ in reactor and increase the H₂ pressure, which can promote the cracking of lignin. Both solid and oil yield in 80% CH₄ concentration experiment were higher than low-level 30% CH₄ experiment. That was because in 80% CH₄, carbon generated by CH₄ cracking increased and the increased H₂ concentration in reactor can increase the yield of oil generated from lignin. The decrease of gas yield matched the result in Chapter 4, the H₂ yield from CH₄ was obviously lower in high-level CH₄ concentration experiment.

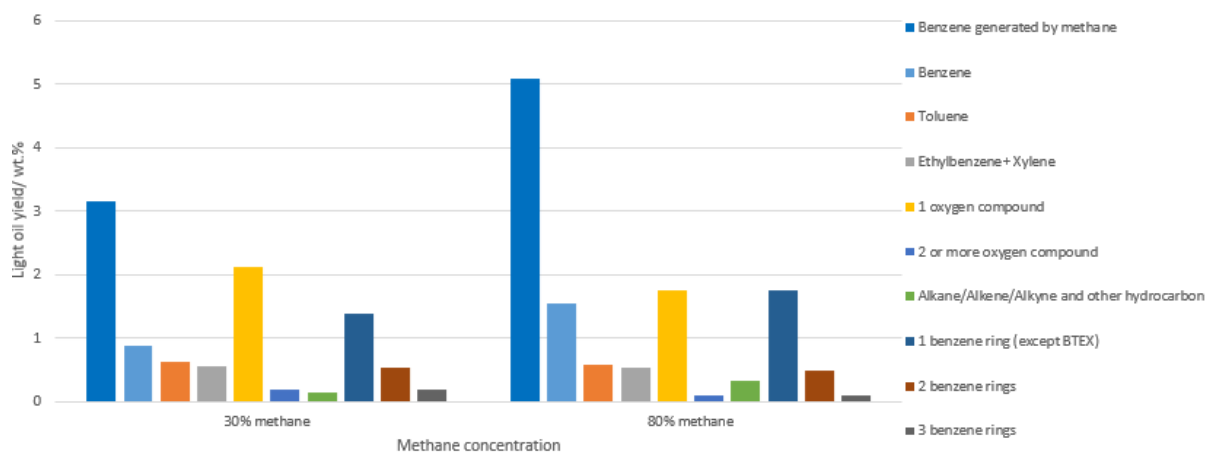
Table 5.17 Products yields and lignin conversion of different CH₄ concentration in inlet gas.

CH ₄ concentration, %	Solid, wt.%	Oil, wt.%	Gas, wt.%	Lignin Conversion, %
30	48.3	25.9	25.8	85.7
80	49.8	27.9	22.3	86.2

As shown in Figure 5.8a, the higher H₂ concentration provided by 80% CH₄ can obviously increase the total light oil yield. The BTEx generated by CH₄ yield increased from 3.16 wt.% in 30% CH₄ experiment to 5.09 wt.% in the 80% CH₄ experiment. The yield of benzene generated by lignin also increased from 2.05 wt.% in 30% CH₄ experiment to 2.65 wt.% in 80% CH₄ experiment. The high H₂ concentration also helped to remove the oxygen from the aromatic rings. The yield of mono-oxygenated compounds decreased from 2.11 wt.% in 30% CH₄ to 1.75 wt.% in 80% CH₄, and the species with two or more oxygens decreased from 0.19 wt.% to 0.085 wt.%. These compounds were turned into BTEx and other 1 benzene ring compounds, which made the yield of compounds with one benzene ring increase from 1.39 wt.% to 1.76 wt.%. Thus, the high level CH₄ concentration was chosen as the optimal condition for CH₄ and lignin simultaneous pyrolysis.



(a)



(b)

Figure 5.8 Light oil yields distribution during pre-oxidated Kraft lignin pyrolysis at 580 °C, 1 bar, 1.5:1 sand:pre-treated lignin, 5g Ni/Al₂O₃-SiO₂ catalyst, 1.15 L min⁻¹ flow rate, 1.5 g min⁻¹ feeding rate (a). group, (b) more detailed disaggregation.

The gas products result is shown in Table 5.18. Due to the significant change on inlet gas composition, the 80% CH₄ experiment had a completely different outlet gas concentration with 30% CH₄. In 80 % CH₄ experiment, the main gas in outlet gas was unreacted CH₄. And in 30% CH₄ experiment, this main gas in outlet gas was background gas N₂. The high H₂ concentration

in 80% CH₄ was from DMA reaction (which was also discussed in Chapter 4). This higher H₂ concentration further promotes the C-O bonds cracking processes and increase the CO and CO₂ concentrations.

Table 5.18 Outlet gas composition in CH₄ concentration experiments. (N₂ background gas)

	30% CH ₄ (vol.%)	80% CH ₄ (vol.%)
H ₂	2.7	16
CO	13.9	17
CO ₂	3.3	4.1
CH ₄	22.8	48.7

5.4.9 Cross Comparison of Different Variables and Structure of Carbon Generated on the Catalyst

In summary, when compared the Run 4 and other experiments operated under 2 L min⁻¹ gas flow rate with Run 12, 13 and other experiments under 1.15 L min⁻¹, the longer residence time allows lignin to be cracked more completely which significantly reduced the yield of large oil molecules that cannot be detected by GC. High pressure can further decrease the yield of oil out of GC range, because high pressure was favored to break C-C and C-O bond and high pressure can inhibit the CH₄ to generate some small molecules. This can also answer why Run 10 had an obviously decrease on yield of out of GC range oil, which had a pressure rise for blockage which was illustrated in Section 5.4.3. The total oil yield of CH₄ and lignin simultaneous pyrolysis experiment had an increasing trend from lowest inert atmosphere and no catalyst to highest 80% CH₄, 1.15 L min⁻¹ gas flow rate. The most important influence was gas flow rate, because the gas flow rate can change the residence time of lignin in reactor. The lignin conversion rate had a similar trend.

An SEM image of catalyst after 80% CH₄ experiment is shown in Figure 5.9. This SEM shows that the main structure of carbon on the catalyst was carbon nanofiber. That means 580 °C and H₂ atmosphere can also promote the carbon deposited in carbon nano fiber structure under CH₄ and lignin simultaneous pyrolysis condition, which also means the Ni catalyst only have limited deactivation caused by deposit carbon, which has been discussed in Chapter 4. Some

agglomerated large particle carbon can still observe in this experiment, that may be char generated from lignin pyrolysis. As illustrated in Chapter 3, under higher temperatures, the amount of this agglomerated large particle carbon from lignin can increase and further made the blockage happened.

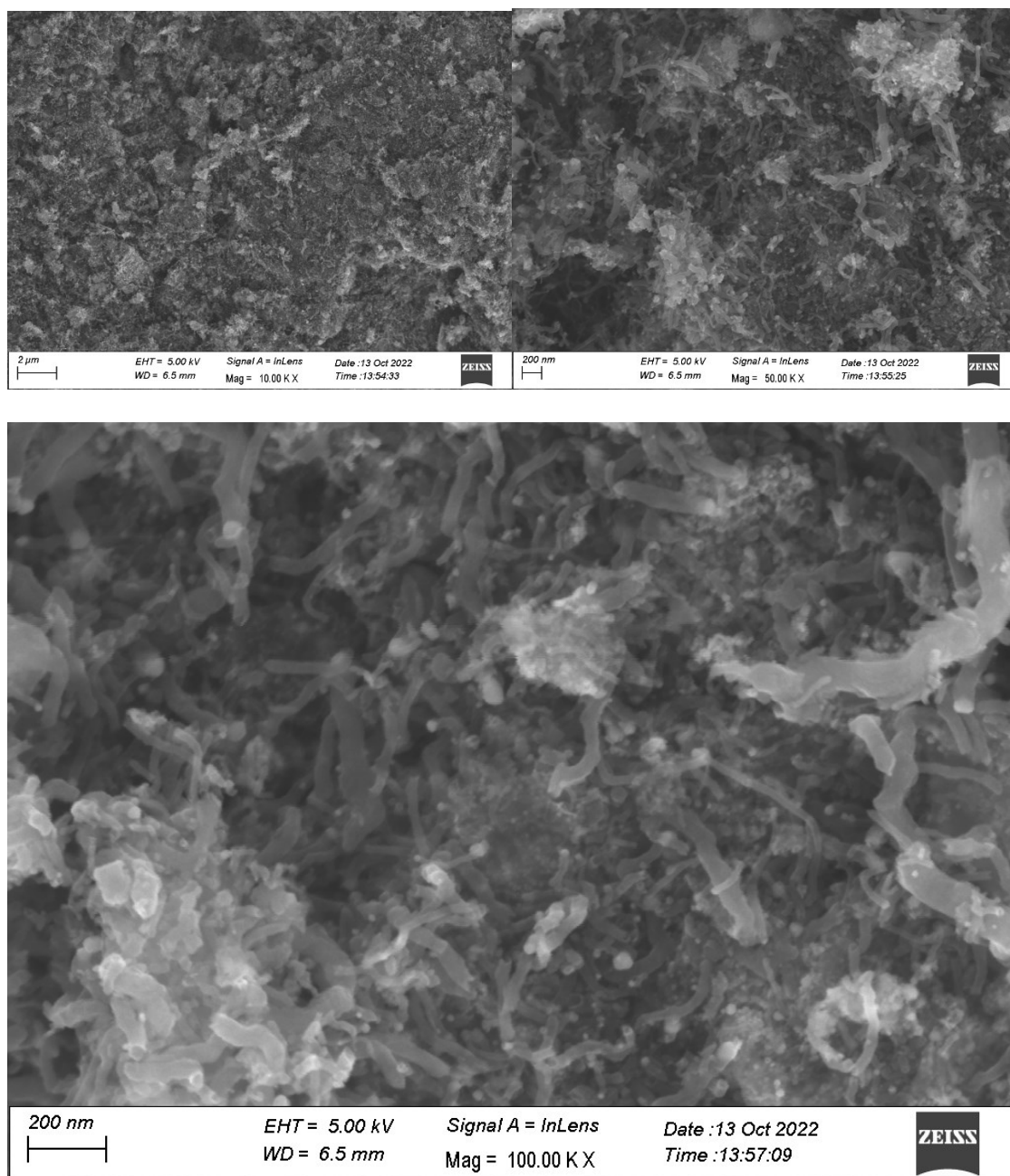


Figure 5.9 SEM image of Ni/Al₂O₃-SiO₂ catalyst, 80% CH₄ and lignin experiment

5.5 Conclusions

The optimal conditions for lignin and CH₄ simultaneous pyrolysis on fluidized bed set up have been studied. The most important influence variable was the residence time of small particle size unreacted lignin and volatile in reactor. To achieve a long residence time, the gas flow rate can be reduced to 1.15 L min⁻¹ which can also carry sand mixed with lignin into reactor. Temperature can also improve the oil yield, however, when the temperature reached 620 °C, blockage would happen. Based on these operating and safety considerations, 580 °C was chosen as the optimal condition. High CH₄ concentration can be beneficial in generating more benzene and improving lignin pyrolysis.

- (1) The agglomeration tests proved that as received lignin from Sigma-Aldrich can block the spout line in a short time under 600 °C. Less feedstock feeding rate, less inlet gas flow rate, and using sand to dilute feedstock lignin were helpful in extending the time before the spout line was blocked. When Ni/Al₂O₃-SiO₂ catalyst was mixed with the bed material, the system can be blocked even under 500 °C. To solve this problem, two pretreatment methods were used in catalytical experiments, which were torrefaction and pre-oxidation. Both methods can extend the time before blockage happens, and the lignin after pre-oxidation can allow the system to operate stably under 580 °C with nearly no blockages.
- (2) The source of H₂ affects the light oil yields and lignin conversion rate. The experiment using external H₂ mixed with N₂ as inlet gas can increase 0.5 wt.% light oil yield from ~1.5 wt.% under pure N₂ as inlet gas experiment. When 30% CH₄ and N₂ as carrier gas, the light oil yields had an obvious increase for oil generated by DMA and in-situ H₂ can further promote the lignin cracking.
- (3) In temperature experiments, 600 °C was found as the best condition to generate highest light oil yield. However, during experiments, the system was at an unstable dynamic condition. Both endothermic and exothermic reactions happened in reactor, that made the reactor temperature can change in a large range before whole system reached steady state. If the reactor temperature reached 620 °C or higher, blockage may happen and stop the feeding. Thus, 580 °C was chosen as the optimal condition to run further

experiments.

- (4) Feeding rate and feedstock dilution rate had relatively small influence on light oil yields. That was because after dilution the amount of pre-oxidated lignin, which was fed into reactor, was not too large. When the feeding rate was too high, a limited blockage, not enough to stop the experiment, can happen in the reactor, increasing its pressure and reducing light oil yields.
- (5) Based on the result obtained from Chapter 4, 3.5 g, rather than 1.56 g, was used as the low-level catalyst amount to compare with the 5 g catalyst. The result showed that more catalyst amount can improve the oil and gas yields in lignin and CH₄ simultaneous pyrolysis experiment.
- (6) The most important variable that affects the oil yield, especially light oil yield, was the gas flow rate. The reason why uses a high gas flow rate at first was that the sand used to dilute the pre-oxidated lignin need a high gas flow rate to feed into reactor. This high gas flow rate can make pre-oxidated lignin to pass the reactor in a short time before it was fully cracked. Thus, lower gas flow rate means longer residence time in this situation. 1.15 L min⁻¹ was chosen as the optimal total flow rate to achieve both feeding requirement and high oil yield. Another way to further extend the residence time was that lengthen the bed length. That can be acquired by having a longer quartz linear and more bed material in fluidized bed or connecting the fluidized bed reactor with another fixed/fluidized bed reactor.
- (7) Higher pressure can obviously reduce the oil and H₂ generated from DMA and CH₄ cracking. However, pressurized condition can promote the hydrocracking process. The results also proved that in high pressure experiments, the oil yield and H₂ concentration reduced, but CO and CO₂ concentrations significantly increased. After comprehensive consideration, atmosphere pressure was chosen as the optimal condition to generate added value oil.
- (8) Higher CH₄ concentration can prove more H₂ for lignin hydrocracking and more light oil from CH₄. That made 80% CH₄ have a better performance on both oil yield and lignin conversion rate than 30% CH₄ in experiments.

Chapter 6. Catalyst Screening for the Simultaneous Pyrolysis of Lignin and CH₄

6.1 Introduction

In experiments described in Chapter 5, it was found that the best performance in terms of lignin and CH₄ simultaneous pyrolysis yields to BTEX and total light oil took place at operating conditions of 580 °C, 1 bar, 1.15 L min⁻¹ of a gas consisting of 80% CH₄, 5 g catalyst in the fluidized bed and 1.5 g min⁻¹ of lignin mass flowrate. However, all the experiments in Chapter 5 were done with Ni/Al₂O₃-SiO₂ as catalyst. Ni catalyst is mainly active towards C-C bond breaking and has limited function on C-O bond breaking process.^[129] This was also backed by the observation shown in Chapter 5 that oxygen-containing compounds were always relatively high under atmosphere pressure, although further deoxygenation was achieved at higher pressures. Further oxygen removal from the oil products and improvement on the total oil and BTEX yield are targeted in the study described in this chapter by using different catalysts in the simultaneous pyrolysis of lignin and CH₄.

Catalysts based metals other than Ni may improve the total and light oil yield. The catalyst used in CH₄ and lignin simultaneous pyrolysis reported in the literature mainly consist of Ni, Mo as active metals.^[129] Previous research showed that the low Ni and Mo concentration catalyst can generate the same level of total oil yield, but Ni catalyst can obtain higher light oil yield and Mo catalyst had a lower alkylphenols yield.^[129, 130]

With this objective, different active metals and supports were tested. These included Mo-Ni, which is known to catalyse C-O bond breaking^[130]; TiO₂ and ZrO₂ catalysts, which are promising as they were proven to lead to more monomeric phenolic compounds during pyrolysis in the absence of H₂^[135, 136, 137]; and Cr₂O₃, which according to previous research can achieve a remarkable light oil concentration in an ex-situ catalytic pyrolysis process.^[138]

The support largely determines the structure and textural properties of the catalyst^[131, 132], and may increase the total oil yield. Al₂O₃ and zeolite have been widely used as lignin pyrolysis catalyst support and contributed to reaching high total oil yields.^[132, 133] Moreover, Ni supported

on Al_2O_3 also had a good performance in the DMA reaction^[134], as observed in Chapter 4. Active carbon fibers (ACF) are another promising catalyst support for lignin pyrolysis as well as carbon nanofibers (CNF). These carbon-based supports were reported to reach high selectivity to phenol and low guaiacol yield when used with Mo as active metal.^[135]

Experiments described in this chapter combined both in-situ (in the fluidized bed) and ex-situ (in a downstream fixed bed) use of catalysts employing the two-stage reactor system described in Chapter 3. In the two-stage configuration, the volatile and intermediate products generated in first stage reactor were carried by the gas flow into a second stage catalytic reactor to explore further upgrading of volatile and intermediate products. The combination of in-situ and ex-situ catalyst is hypothesized to increase the BTEX yield.

In this chapter, four different sections are used to discuss the effect of different catalysts on lignin and CH_4 co-pyrolysis. The following section (Section 6.2) illustrates the experimental conditions applied. Section 6.3 describes the effect of different catalysts on the product distributions. Two catalysts composed of 20% Ni on different supports (Al_2O_3 and ACF) were first used to test the influence of these two supports under the same metal concentration. Then, two Mo-Ni catalyst which had similar Ni concentrations (7.2% and 7.9%) and different Mo concentrations (18.5% and 38.6%) on the same support (Al_2O_3) were used to test the effect of Mo concentration on oil yield and characteristics. To complete this section, three catalysts based on different metals, $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, TiO_2 and ZrO_2 as catalytic sites were tested. The effect of reactor configuration with in-situ and ex-situ placement of the catalyst is also discussed in Section 6.3. Finally, conclusions are presented in Section 6.4.

6.2 Experimental Conditions

Both commercial and in-house developed catalysts were used in this work. Commercial ones included two massive Ni catalysts with smaller amounts of SiO_2 and Al_2O_3 , two Ni-Mo supported on Al_2O_3 , a $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, TiO_2 and ZrO_2 (with a small content of Hf, which occurs naturally with Zr and is of difficult separation). Catalysts developed in the group's laboratories consisted of the Ni catalysts supported on Al_2O_3 and activated carbon fibers (ACF), prepared by Mr. Jiaxian Luo and Dr. Guanming Yuan, respectively. The full composition of all catalysts

is presented in Table 6.1. All commercial catalyst pellets (which fit to be directly used in industrial case. The in-house developed lab used catalyst should also be made into pellets before it was used in industrial case) were first ground into powder form and sieved to suitable particle size (between 200 to 300 μm) for the experiments.

Table 6.1 Catalyst information of in-situ catalyst experiment under 580 °C, 1 bar, 80% CH₄, 1.5:1 sand:pre-treated lignin, 5g catalyst, 1.15 L min⁻¹ flow rate, 1.5 g min⁻¹ feeding rate.

Name	Catalyst active site	Catalyst support
Ni/Al ₂ O ₃ -SiO ₂	80% Ni	4.6% Al+8% Si
Ni/SiO ₂	66% Ni	1.5% Al+28.6% Si
Ni/Al ₂ O ₃	20% Ni	Al ₂ O ₃
Ni/ACF	20% Ni	ACF
low-MoNi/Al ₂ O ₃	18.5% Mo+7.2% Ni	72.9% Al
high-MoNi/Al ₂ O ₃	38.6% Mo+7.9%Ni	47.2% Al
Cr ₂ O ₃ /Al ₂ O ₃	33.5% Cr	65.4% Al
TiO ₂	98% Ti	/
ZrO ₂	96% Zr+2.4% Hf	/

As illustrated above, all as-received commercial catalysts were in pellets of at least 1 cm diameter or length. The pictures shown in Figure 6.1 are all after grinding. The reduction process of all catalysts was described in Chapter 3. Two Mo-Ni catalyst had light green color before reduction and after reduction all their color turns into black which means the Mo and Ni were mainly exist in oxides and these oxides can be effectively reduced during reduction process. That also matched with the XRD result shown in Figure 6.2. The as-received Cr catalyst had a green color (Cr₂O₃) and this green went deeper after reduction^[149] (which also matched with XRD result that after reduction the Cr₂O₃ nearly cannot be reduced). All other catalysts did not have color or shape difference between as-receive and after reduction.

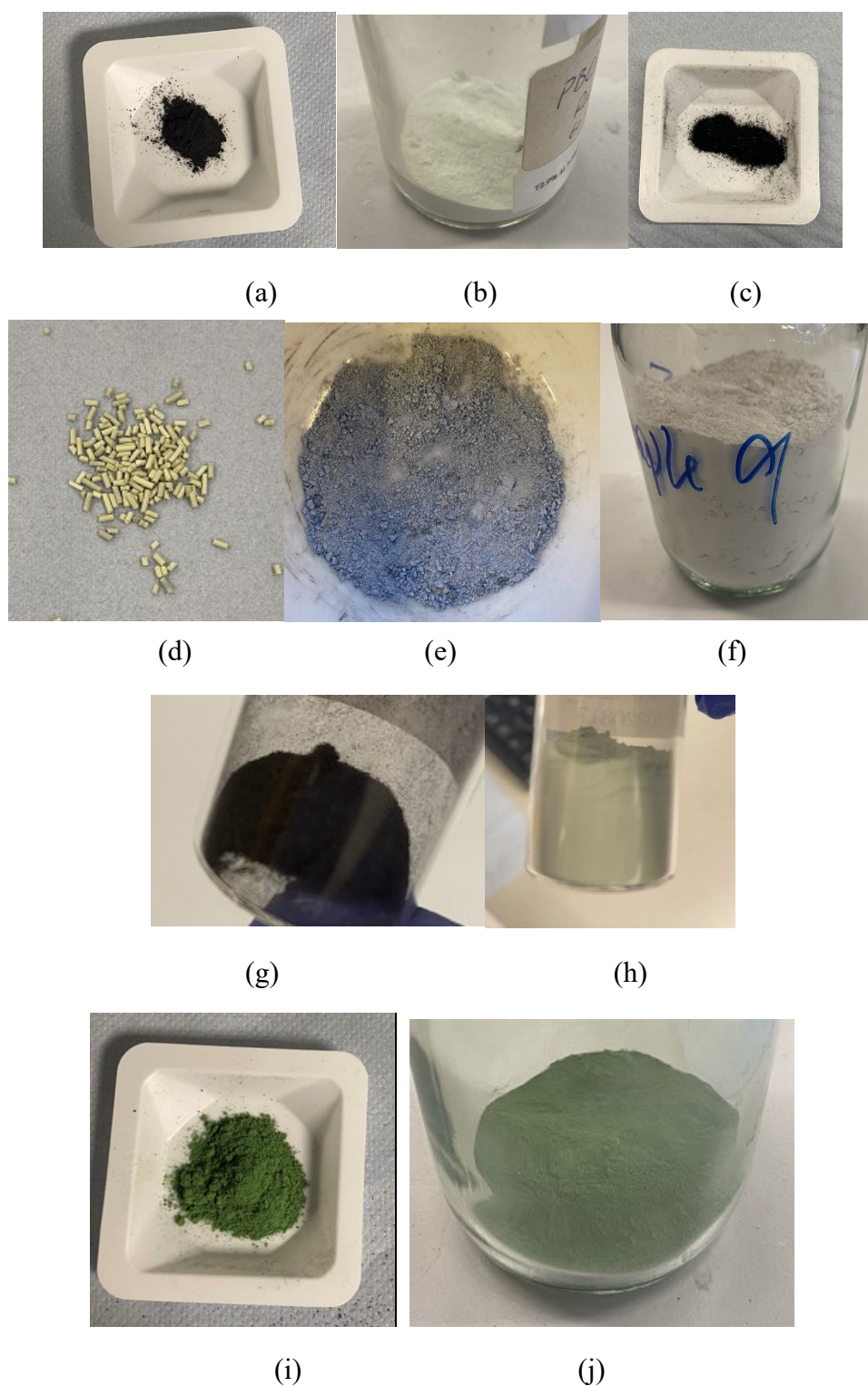


Figure 6.1 Catalysts used in this chapter 6 as received and reduced (a. low-MoNi/Al₂O₃ reduced, b low-MoNi/Al₂O₃ as received, c. high-MoNi/Al₂O₃ reduced, d. high-MoNi/Al₂O₃ 33.5% as received, e. 96% ZrO₂ as received, f. 98% TiO₂ as received, g. Ni/ACF, h. Ni/Al₂O₃, i. 33.5% Cr₂O₃/Al₂O₃ reduced, j, Cr₂O₃/Al₂O₃ as received)

As mentioned above, some experiments were carried out with a fixed bed reactor placed downstream from the fluidized bed, in a configuration shown in Chapter 3. This allowed the placement of some catalyst in an ex-situ configuration where it is in contact with the volatiles produced in the fluidized bed rather than with the full lignin and CH₄ feed. Experiments are described in Table 6.2. The total amount of Ni catalyst was kept constant at 5 g. In some experiments this was distributed between fluidized and fixed bed reactor with 2.5 g catalyst each while in others all the catalyst was placed in the downstream fixed bed.

Table 6.2 Experimental conditions of two-stage bed system. All runs were performed with Ni/Al₂O₃-SiO₂ as catalyst in the fixed bed, at 580 °C, 1 bar, 5g catalyst in total between the two beds, 80% CH₄ in a gas with total flow rate of 1.15 L min⁻¹ and 1.5 g min⁻¹ solid feeding rate.

Run	Fluidised bed catalyst	Fixed bed catalyst weight (g)	Solid Feedstock
10	None	5	None
11	None	5	Sand:lignin=1.5:1
12	Ni/Al ₂ O ₃ -SiO ₂	2.5	None
13	Ni/Al ₂ O ₃ -SiO ₂	2.5	Sand:lignin=1.5:1

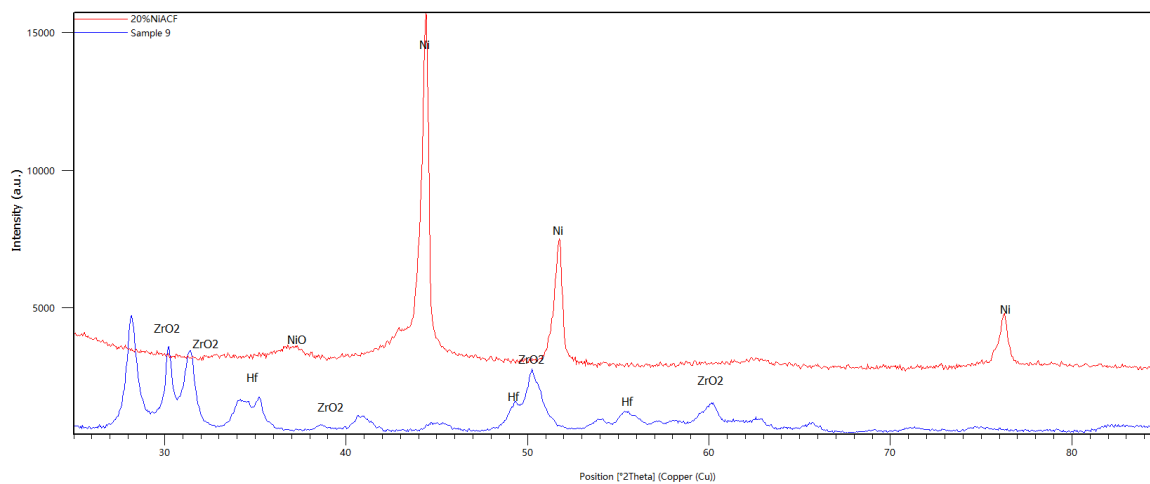
As in Chapter 5, the light oil (GC-detectable fraction of the oil) and gas products were analysed by GC-FID&MS and GC-TCD. TGA was used to detect the weight of coke generated in the experiment. Equations used in the calculations were also the same as in Chapter 5 and have been introduced in Chapter 3 (Equations 3.12, 3.13, 3.17 and 3.18).

6.3 Results and Discussion

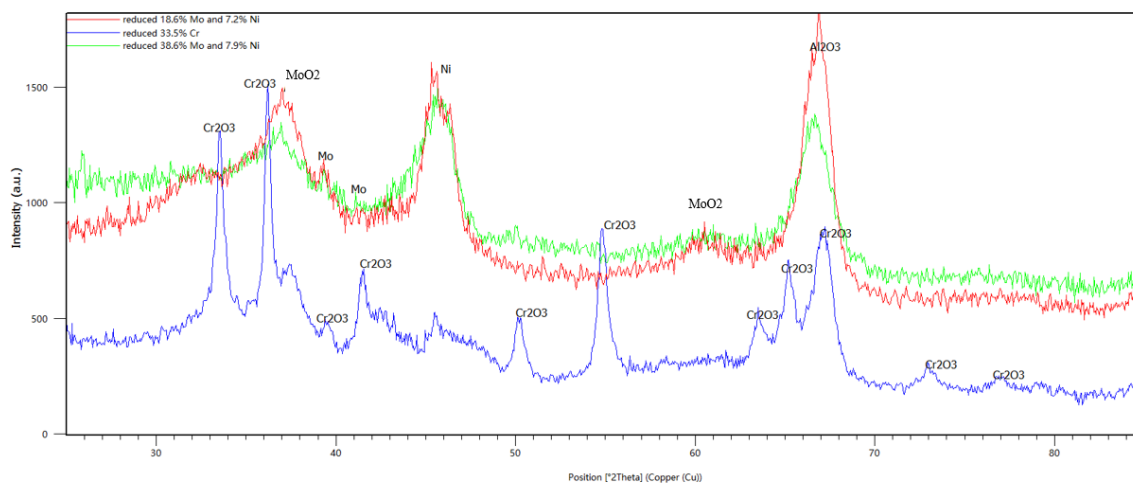
6.3.1 Catalyst Characterization

The XRD results of all catalysts used in this study are given in Figure 6.2. Unlike the HZSM-5 and Ni/SiO₂ catalyst shown in Chapter 4, all of these catalysts had very clear crystalline peaks and high enough peak intensity for metal and metal oxides. All Ni in as received Ni catalysts was in NiO state. Among these catalysts, after the catalyst reduction process illustrated in

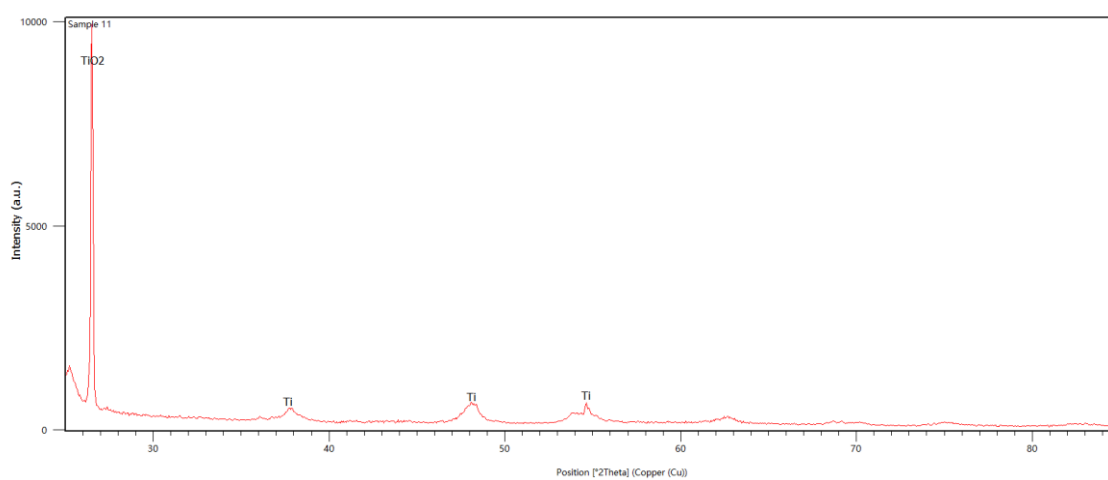
Chapter 3, only Ni/ACF catalyst could be fully reduced to pure metal. Part of Ni/Al₂O₃, low-MoNi/Al₂O₃, high-MoNi/Al₂O₃ and TiO₂ catalyst can be reduced to elemental metal. For ZrO₂ and Cr₂O₃/Al₂O₃ catalyst, the metal oxide cannot be completely reduced by the method used in this study.



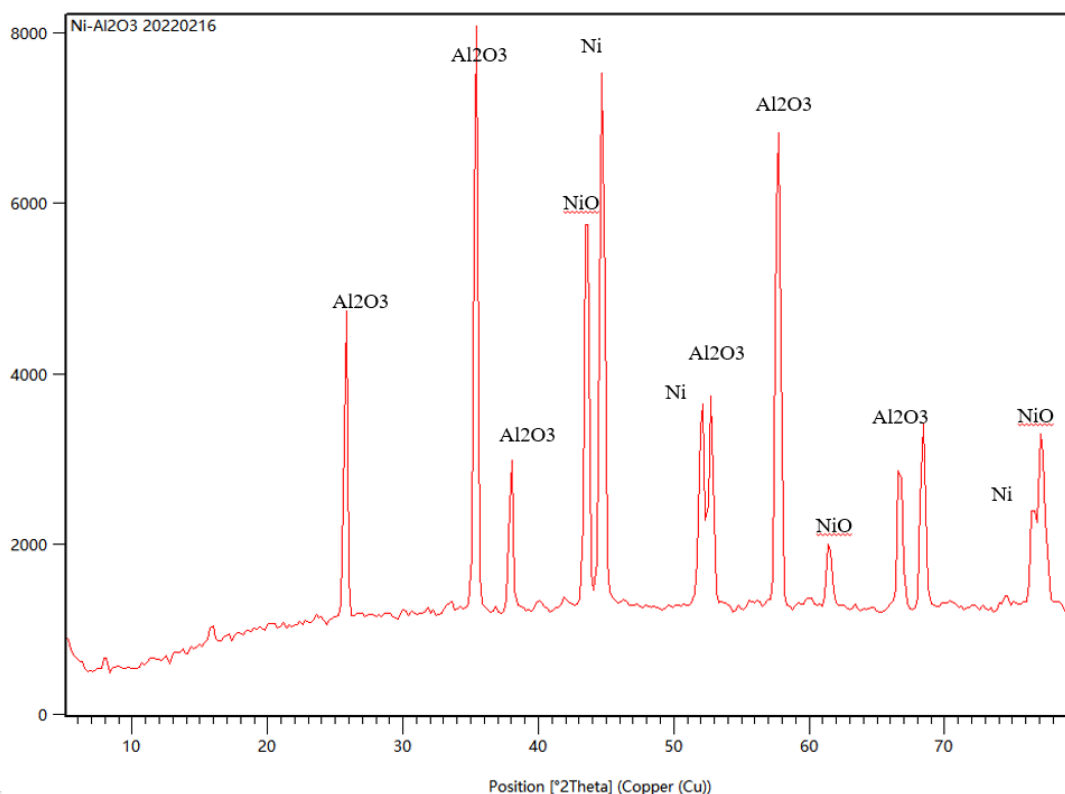
(a)



(b)



(c)



(d)

Figure 6.2 XRD patterns of (a) reduced Ni/ACF and ZrO₂ (sample 9), (b) reduced low-MoNi/Al₂O₃, Cr₂O₃/Al₂O₃, high-MoNi/Al₂O₃, (c) reduced TiO₂ (sample 11), (d) reduced Ni/Al₂O₃.

The XRF spectra of all catalysts are given in Appendix 5. According to the XRF result, all catalysts had a low impurity content. The active metal and support element concentrations add-up of all catalysts were higher 95%. Ca and Fe were the main impurity in all catalysts (both of them usually had a concentration lower than 1%). Based on XRD and DMA experiments result, the XRF result may have an essential error on Ni/SiO₂ catalyst. And the Ni/SiO₂ must had a bad crystal structure and heterogeneous.

The BET results of all catalysts used in this chapter are given in Table 6.3. The Ni/ACF had the highest 798.9 m² g⁻¹ specific surface area and 0.7 cm³ g⁻¹ pore volume. The low-MoNi/Al₂O₃ had the highest 16.6 nm pore size. However, Ni/ACF had a low density and flocculent shape catalyst and therefore it was crucial to test its performance in the fluidized bed reactor. The Ni/Al₂O₃ catalyst had an extremely low specific surface area and pore volume. That might because the in-house making process of this catalyst was not ideal or the Al₂O₃

source used as support was not good enough.

Table 6.3 Textural properties (specific surface area, pore volume and average pore diameter) of reduced catalysts.

Sample	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	Pore Size (nm)
Ni/ Al_2O_3	3.87	0.04	12.0
Ni/ACF	798.9	0.7	4.1
low-MoNi/ Al_2O_3	125.1	0.6	16.6
high-MoNi/ Al_2O_3	173.2	0.5	10.8
$\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$	54.6	0.2	13.8
TiO_2	143.6	0.4	10.8
ZrO_2	51.4	0.1	8.2

The hysteresis loops of catalysts used in this chapter are shown in Figure 6.3. Both branches of the loop in Ni/ Al_2O_3 nearly do not exhibit any difference during the BET isothermal testing process, showing a very low adsorbed quantity. This catalyst has very low surface area and extremely simple pore structure. On the other hand, the Ni/ACF catalyst showed a very high adsorbed quantity and a clear H2(b) type hysteresis loop, evidence of a very large surface area and complicated pore structure. Some pores in Ni/ACF are blocked and other open pores have a large neck width distribution. This large difference was caused by the different support. Another interesting hysteresis loop was obtained in ZrO_2 catalyst analysis. This kind hysteresis loop belongs to type H5 loop, which is very unusual ^[139] according to IUPAC. Such loop suggests a distinctive structure containing both open and partially blocked mesopores, which may have caused the low pore volume in ZrO_2 catalyst.

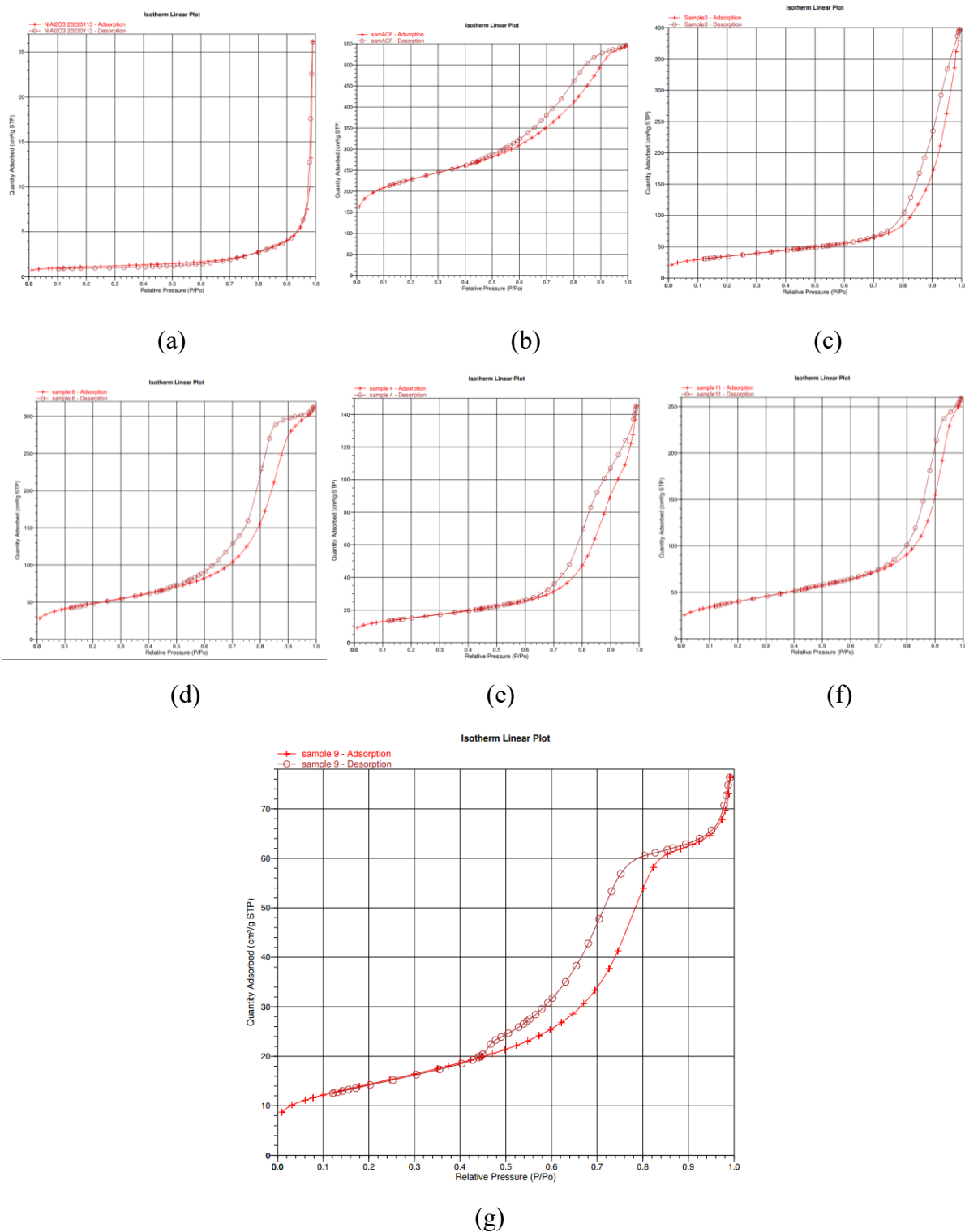


Figure 6.3 Hysteresis loops of (a) Ni/Al₂O₃, (b) Ni/ACF, (c) low-MoNi/Al₂O₃, (d) high-MoNi/Al₂O₃, (e) Cr₂O₃/Al₂O₃, (f) TiO₂, (g) ZrO₂.

6.3.2 Performance of Ni-based Catalysts

The performance of Ni/Al₂O₃-SiO₂ catalyst in experiments carried out with two CH₄ inlet concentrations, 30% and 80%, was discussed in Chapter 5. In this section, the performance of different Ni-based catalysts will be illustrated.

6.3.2.1 Performance of Ni/SiO₂ and Ni/Al₂O₃-SiO₂

The performance of Ni/SiO₂ and Ni/Al₂O₃-SiO₂ catalysts was tested in the simultaneous pyrolysis of lignin and CH₄. As illustrated in Chapter 5, the gas yield was calculated by difference based on the yields of solid and oil. The Ni/Al₂O₃-SiO₂ catalyst had better performance on all oil, gas yield and lignin conversion rate than Ni/SiO₂, as shown in Table 6.4. Based on the results in Chapter 4, Ni/SiO₂ catalyst does not significantly catalyze the DMA reaction, which is likely due to its low surface area and unstable crystal structure. That may make Ni/SiO₂ unable generate enough H₂ to promote a greater degree of lignin pyrolysis. This assumption was reinforced by the results shown in Table 6.4, where this catalyst leads to higher solid and lower oil yield.

Experiments with Ni/Al₂O₃-SiO₂ catalyst achieved 86.2% lignin conversion with 50.2 wt.% combined total oil and gas yields. According to previous research, the solid yield of lignin and CH₄ simultaneous pyrolysis was higher than 50% in most cases,^[129, 140] due to CH₄ cracking generating additional carbon deposits.

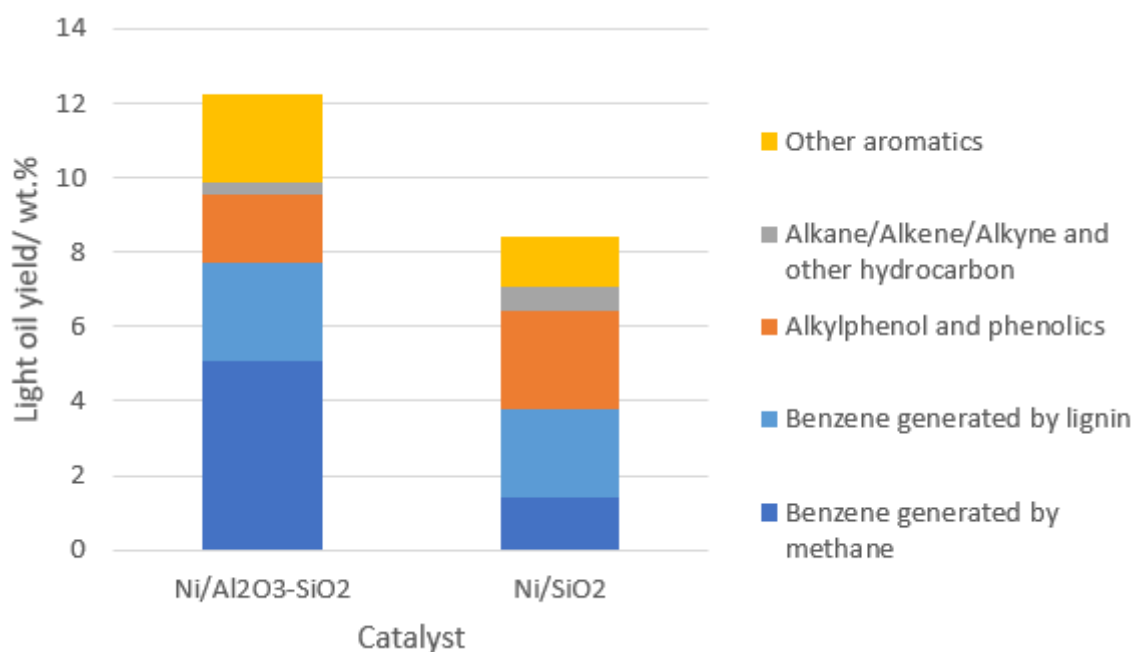
Table 6.4 Products yields and lignin conversion with Ni/SiO₂ and Ni/Al₂O₃-SiO₂ catalysts.

Catalyst	Solid, wt.%	Oil, wt.%	Gas, wt.%	Lignin Conversion, %
Ni/Al ₂ O ₃ -SiO ₂	49.8	27.9	22.3	86.2
Ni/SiO ₂	62.2	20.6	17.2	80.6

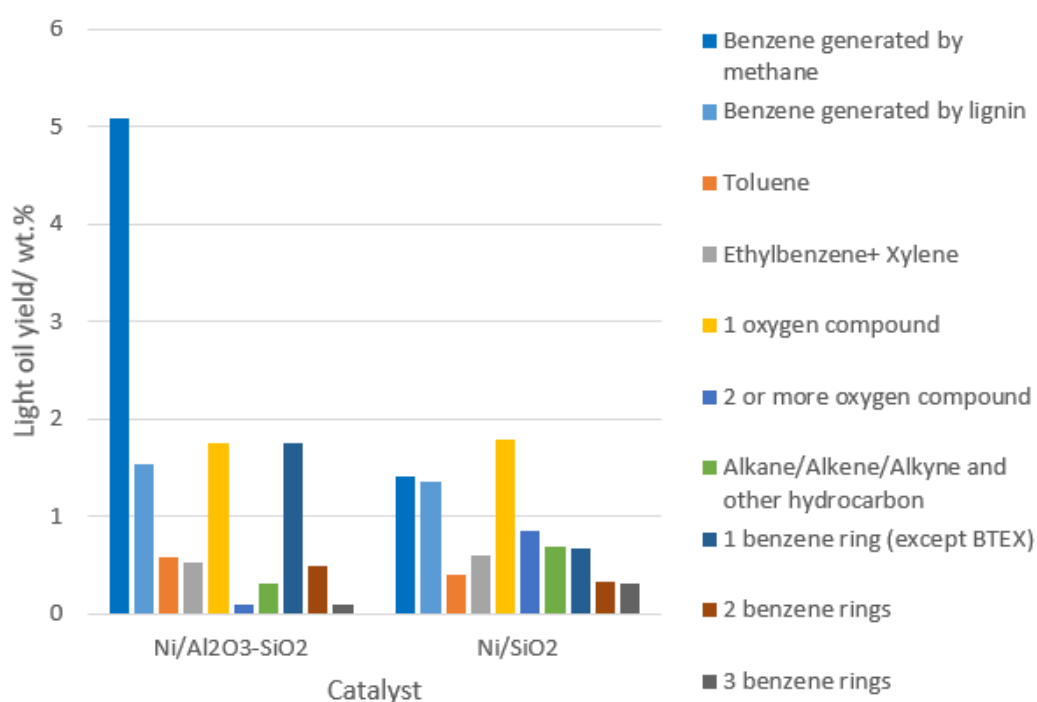
Figure 6.4 shows that Ni/Al₂O₃-SiO₂ catalyst had good performance in terms of light oil yield both from DMA (5.09 wt.%) and lignin pyrolysis (7.1 wt.%). The latter is similar to the light oil generated from lignin with Ni/SiO₂ as catalyst (7.0 wt.%). The light oil generated from lignin with Ni/Al₂O₃-SiO₂ catalyst was composed of 2.6 wt.% BTEX and 1.8 wt.% other

monoaromatics. Polyaromatics and other non-aromatic hydrocarbons, which were not target products and have lower added values, were very low in the Ni/Al₂O₃-SiO₂ catalyst experiment. (0.085 wt.% and 0.31 wt.%, respectively).

The performance of Ni/SiO₂ catalyst in generating target BTEX and monoaromatics from lignin was not as good. The BTEX yield from lignin using Ni/SiO₂ as catalyst was 2.3 wt.% and the monoaromatics yield was only 0.67 wt.%, even lower than the 0.84 wt.% yield of polyaromatics and 0.69 wt.% yield of non-aromatic hydrocarbons. The BTEX yield generated by CH₄ in Ni/SiO₂ experiment was also low at only 1.4 wt.%, as discussed in Chapter 4. The low surface area, ill-defined crystal structure and pore blockages were the main reasons for the lower activity of Ni/SiO₂ catalyst in comparison with Ni/Al₂O₃-SiO₂. The cross comparison of these two catalysts will be illustrated in the following section.



(a)



(b)

Figure 6.4 Light oil yields distribution during pre-oxidated Kraft lignin pyrolysis at 580 °C, 1 bar, 80% CH₄, 1.5:1 sand:pre-treated lignin, 5 g catalyst, 1.15 L min⁻¹ flow rate, 1.5 g min⁻¹ feeding rate. (a). group, (b) more detailed disaggregation.

The gas products composition is shown in Table 6.5. As shown in Chapter 4, the Ni/Al₂O₃-SiO₂ catalyst had a good H₂ generation performance in the DMA reaction, which affected the H₂

availability during the simultaneous pyrolysis of lignin and CH_4 . Ideal H_2 concentration also increased the concentration of CO and CO_2 by the process of H_2 removing the oxygen in lignin. The low H_2 concentration in the presence of Ni/SiO_2 was mainly due to its bad performance on DMA reaction, as discussed above and in Chapter 4. The low CO and CO_2 concentrations matched with the result shown in Figure 6.4 that the alkylphenol and phenolics had a high proportion in light oil yield. The Ni/SiO_2 catalyst had very limited function on remove oxygen from cracked lignin intermediate compounds.

Table 6.5 Outlet gas composition at steady state in Ni catalyst experiments. (N₂ as background gas)

	Ni/Al ₂ O ₃ -SiO ₂ (vol.%)	Ni/SiO ₂ (vol.%)
H ₂	16	9.1
CO	17	10.5
CO ₂	4.1	3.4
CH ₄	48.7	56.8

6.3.2.2 Performance of Supported Ni Catalysts: Ni/Al₂O₃ and Ni/ACF

As discussed above, two catalysts with 20% Ni on Al₂O₃ and active carbon fiber (ACF) were synthesized, enabling a comparison on the performance of these two supports. Different supports can provide different surface area and chemical properties, such as acidity needed for cracking, as well as affect the loading of Ni active sites.

Both Ni/Al₂O₃ and Ni/ACF had a very low lignin conversion, given in Table 6.6 along with the product yields. The Ni/Al₂O₃ catalyst had worse textural properties (including extremely low surface area and pore volume), which might have affected the conversion of CH₄ through DMA, making less H₂ available for the lignin depolymerization reaction. Moreover, the greater acidity of alumina in comparison with carbon supports is likely to have played a role in the higher solid yield.

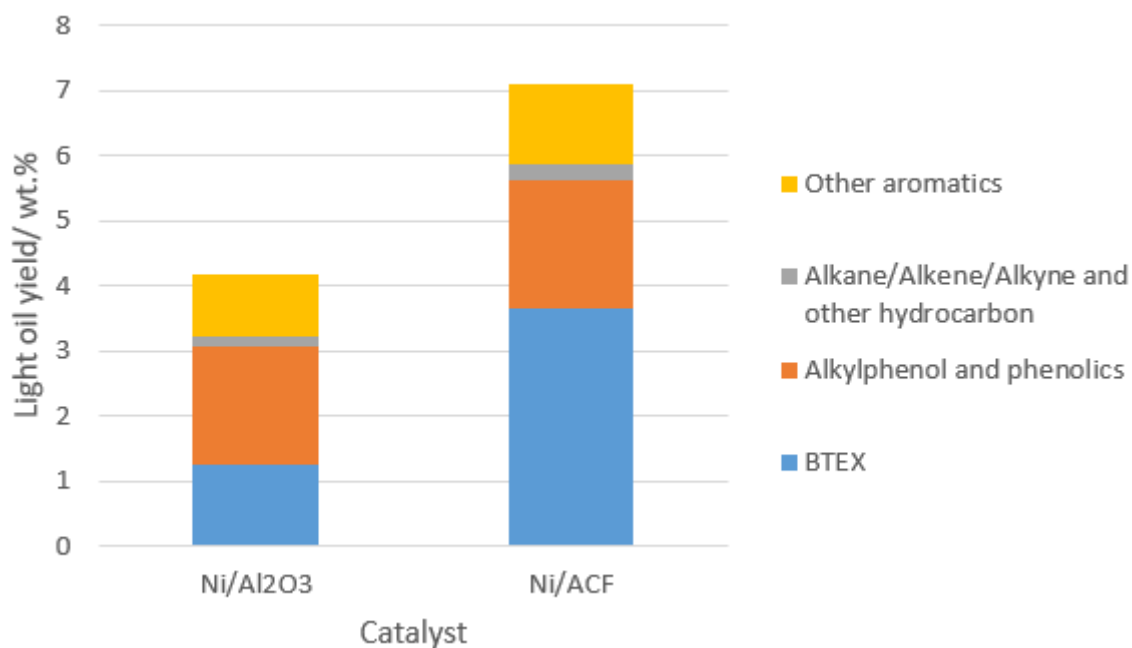
While the Ni/ACF catalyst led to a higher oil yield, its very low density and flocculent shape made it easy to be carried away from the reactor by the fluidizing gas. After the experiment, some catalyst was collected at the end of the reactor tube, on the inner face of the sealed flange and at the tar trap entrance. This loss of catalyst may have limited lignin conversion and affected product yields.

Table 6.6 Products yields and lignin conversion of Ni/Al₂O₃, Ni/ACF catalysts.

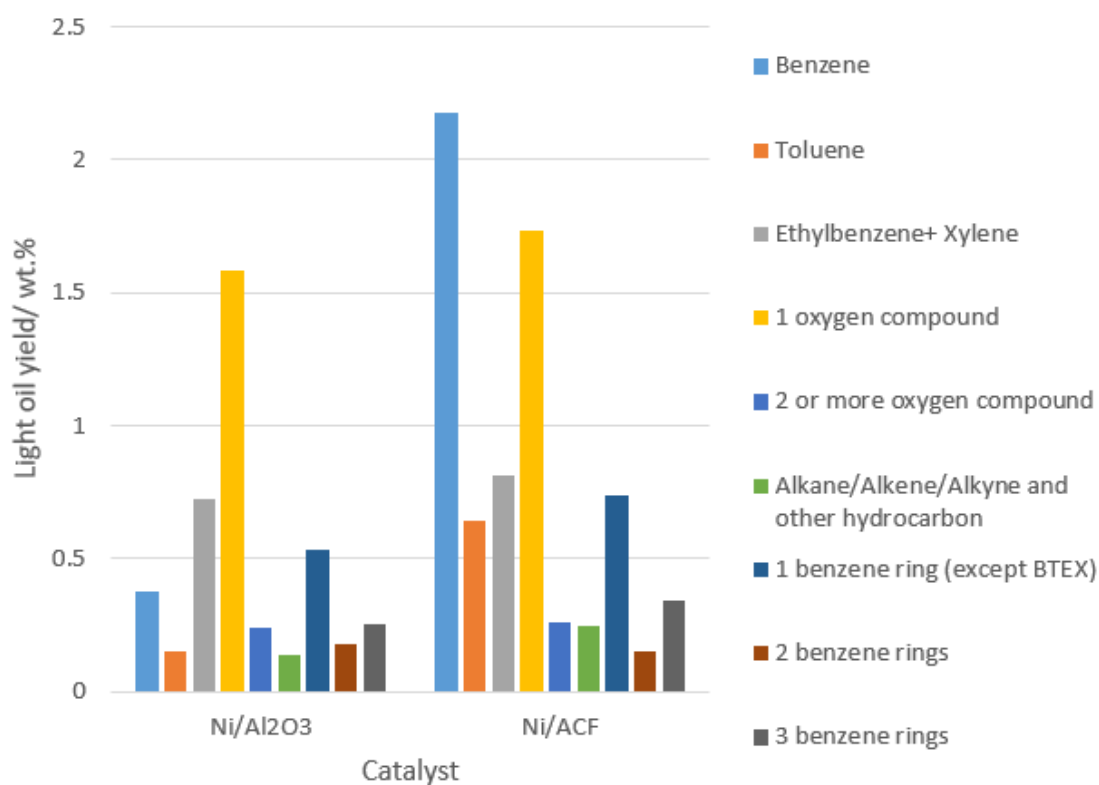
Catalyst	Solid, wt.%	Oil, wt.%	Gas, wt.%	Lignin Conversion, %
Ni/Al ₂ O ₃	69.0	15.6	15.4	73.5
Ni/ACF	63.1	19.2	16.9	79.0

The light oil yield and composition obtained in these two experiments are given in Figure 6.5. The ACF-supported catalyst produced a 7.1 wt.% light oil yield, which is lower than obtained with the massive Ni catalysts shown in the previous section. This light oil had good benzene and toluene yields (2.2 wt.% and 0.64 wt.%, respectively). The use of Ni/Al₂O₃ resulted in lower light oil yields (4.2 wt.%), with particularly low benzene and toluene yields of 0.38 wt.% and 0.15 wt.%, respectively. On the other hand, the yields of other light oil components like phenols and derivatives were similar for both catalysts.

It is thought that the low specific surface area and pore volume of Ni/Al₂O₃ may have hindered H₂ generation by DMA. Moreover, according to the XRD result shown in Figure 6.3, this catalyst still had NiO after reduction, which has been shown in Chapter 4 to have a worse performance in DMA than the reduced form of Ni. On the other hand, Ni/ACF has very large specific surface area, pore volume and average pore diameter, which makes the active sites highly accessible to the lignin macromolecule. The gas product compositions are shown in Table 6.7. Ni/Al₂O₃ only generates very limited H₂, CO and CO₂.



(a)



(b)

Figure 6.5 Light oil yields distribution during pre-oxidated Kraft lignin pyrolysis at 580 °C, 1 bar, 80% CH₄, 1.5:1 sand:pre-treated lignin, 5g 20% Ni catalyst, 1.15 L min⁻¹ flow rate, 1.5 g min⁻¹ feeding rate. (a) grouped, (b) more detailed disaggregation.

Table 6.7 Outlet gas composition in different support catalyst experiments. (N₂ as background gas)

	Ni/Al ₂ O ₃ as support (vol.%)	Ni/ACF as support (vol.%)
H ₂	3.5	8.7
CO	4.4	10.1
CO ₂	1.4	4.3
CH ₄	67.6	54.6

6.3.3 Performance of Mo-Ni Based Catalysts

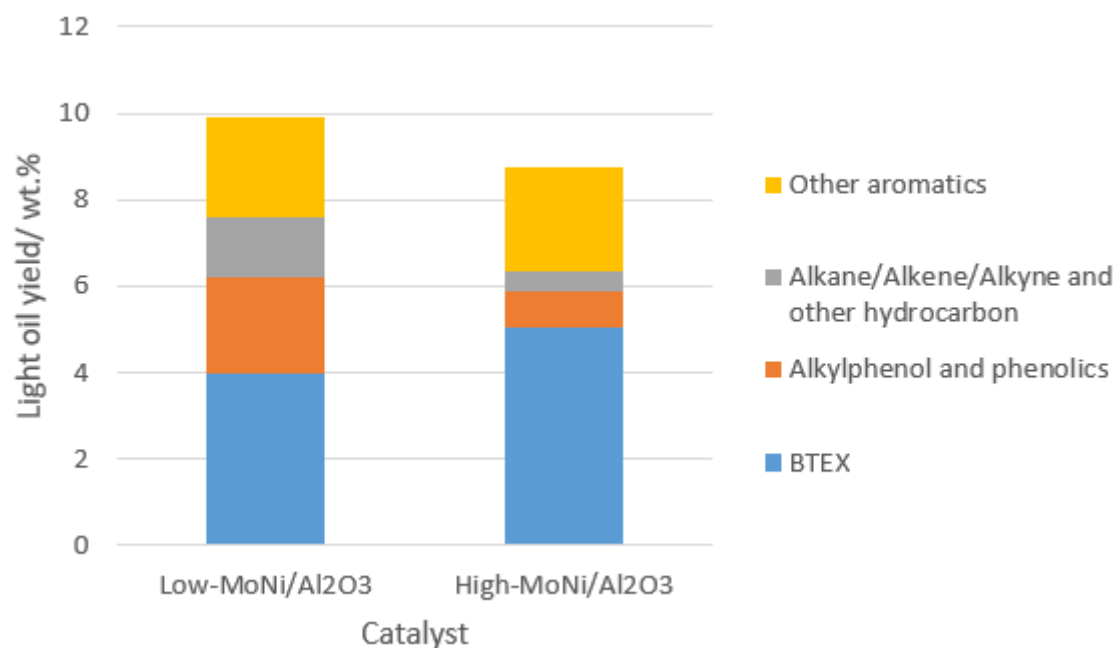
In this section, two Mo-Ni based catalysts supported on Al₂O₃ which had different Mo concentrations (18.5% and 38.6%) and similar Ni concentrations (7.2% and 7.9%) are compared in lignin and CH₄ simultaneous pyrolysis experiments. Based on the results in Table 6.8, both Mo-Ni catalysts had very similar yields for all fractions with a slightly better performance for the one with high-Mo loading.

The detailed characterization of light oil is shown in Figure 6.6. The Mo-Ni catalysts had lower light oil yield than Ni/Al₂O₃-SiO₂ but higher than other Ni-based catalysts. The comparison is particularly interesting with Ni/Al₂O₃ as the Mo-Ni/Al₂O₃ catalysts have a lower Ni loading but add the presence of Mo. Both Mo-Ni/Al₂O₃ reached higher conversions than Ni/Al₂O₃ (similar to the Ni/Al₂O₃-SiO₂ catalyst) and led to lower solid and higher oil and gas yields, which suggests that Mo had catalytic activity towards lignin depolymerization. This seems to be particularly the case in the deoxygenation of the lignin derivatives, as can be seen by the comparison between the light oil oxygen contents. The yield of mono-oxygenated alkylphenol and phenols in low-MoNi/Al₂O₃ catalyst was 0.81 wt.% while high-MoNi/Al₂O₃ achieved a greater reduction to 0.36 wt.%. Both values were lower than the those obtained with Ni-only catalysts, which was 1.6 wt.% in Ni/Al₂O₃ catalyst. However, the low-MoNi/Al₂O₃ catalyst experiment had a high yield of species with two or more oxygens (1.4 wt.%) and non-aromatic hydrocarbons (1.36 wt.%). The light oil yield for unit mass (1 g) Mo in low-MoNi/Al₂O₃ was 10.7 wt.% and that number for high-MoNi/Al₂O₃ was 4.5 wt.%. The BTEX yield for unit mass (1 g) Mo in low-MoNi/Al₂O₃ was 4.3 wt.% and for high-MoNi/Al₂O₃ was 2.6 wt.%. Although

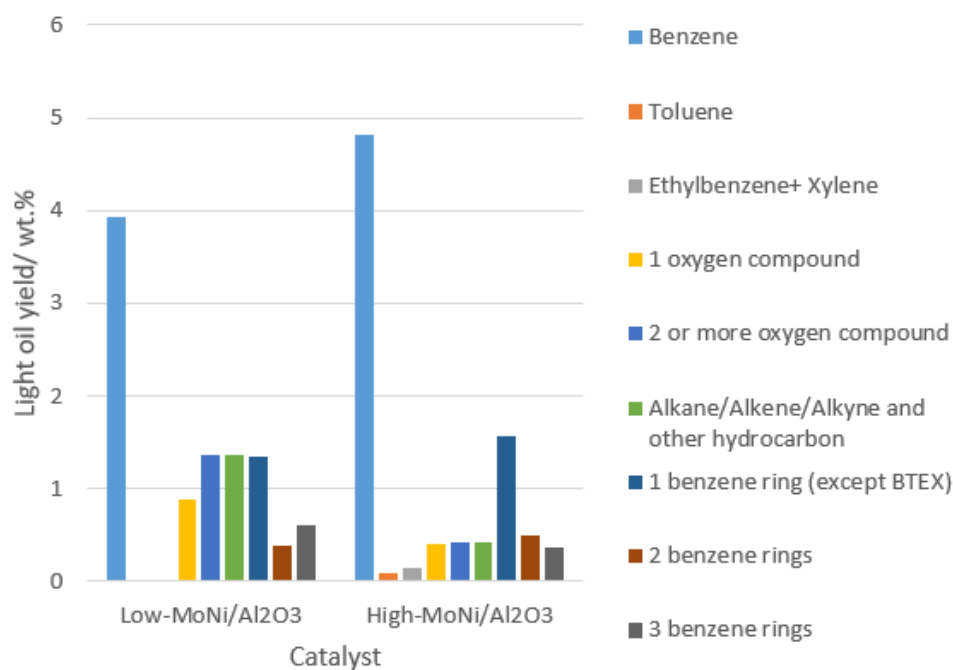
the unit Mo oil yield of low-MoNi/Al₂O₃ was higher than high-MoNi/Al₂O₃, the low-MoNi/Al₂O₃ had less Mo in unit mass catalyst. That means the low-MoNi/Al₂O₃ need higher amount of weight to achieve the same Mo amount with high-MoNi/Al₂O₃, which will further affect the bed length.

This higher level of deoxygenation high-MoNi/Al₂O₃ was achieved in parallel to a slightly higher gas yield as well as greater CO and CO₂ concentrations in the product gas, as shown in Table 6.9. In line with these results, the high-MoNi/Al₂O₃ showed higher yield of BTEX (6.0 wt.% vs. 5.3 wt.%) and other monoaromatics (1.6 wt.% vs. 1.4 wt.%) than low-MoNi/Al₂O₃. Table 6.8 Products yields and lignin conversion of low-MoNi/Al₂O₃, high-MoNi/Al₂O₃ catalysts.

Catalyst	Solid, wt. %	Oil, wt. %	Gas, wt. %	Lignin Conversion, %
low- MoNi/Al ₂ O ₃	53.6	22.9	23.5	83.1
high- MoNi/Al ₂ O ₃	52.2	23.7	24.1	85.6



(a)



(b)

Figure 6.6 Light oil yields distribution during pre-oxidated Kraft lignin pyrolysis at 580 °C, 1 bar, 80% CH₄, 1.5:1 sand:pre-treated lignin, 5g Mo & Ni catalyst, 1.15 L min⁻¹ flow rate, 1.5 g min⁻¹ feeding rate. (a). group, (b) more detailed disaggregation.

Table 6.9 Outlet gas composition in Mo catalyst experiments (N₂ as background gas)

	low-MoNi/Al ₂ O ₃ (vol.%)	high-MoNi/Al ₂ O ₃ (vol.%)
H ₂	5.4	6.2
CO	12.5	13.1
CO ₂	9.2	9.7
CH ₄	52.1	50.5

6.3.4 Performance of Cr₂O₃/Al₂O₃, TiO₂ and ZrO₂

The performance of three catalysts with high metal loading, Cr₂O₃/Al₂O₃, TiO₂ and ZrO₂, were tested in simultaneous KL and CH₄ pyrolysis. Cr- and Ti-based catalysts were tested in previous studies, but typically at low concentrations.^[136, 138] Zr was selected as a promising metal due to its similar properties as Ti.

Some interesting results can be found in Table 6.10. Experiments with TiO₂ and ZrO₂ led to relatively low gas yields. It can be speculated first, that the good adsorption for H₂ at high temperatures shown by Ti and Zr^[141, 142, 143] made the H₂ generated by CH₄ not fully available for lignin upgrading. Second, both Ti and Zr catalysts had poor performance towards C-O bond breaking as suggested by the yields of oxygenated compounds in Figure 6.7(a).

The Cr₂O₃/Al₂O₃ catalyst showed the lowest total oil yield among these three catalysts (only higher than two 20% Ni catalyst). This catalyst had low surface area and pore volume and in addition, it has been reported that Cr₂O₃ ability to break C-C bonds is limited without other metal sites, according to previous lignin pyrolysis research that concluded that mixing Cr₂O₃ with Fe enhanced the catalytic activity.^[138]

Table 6.10 Products yields and lignin conversion of Cr₂O₃/Al₂O₃, TiO₂, ZrO₂ catalysts.

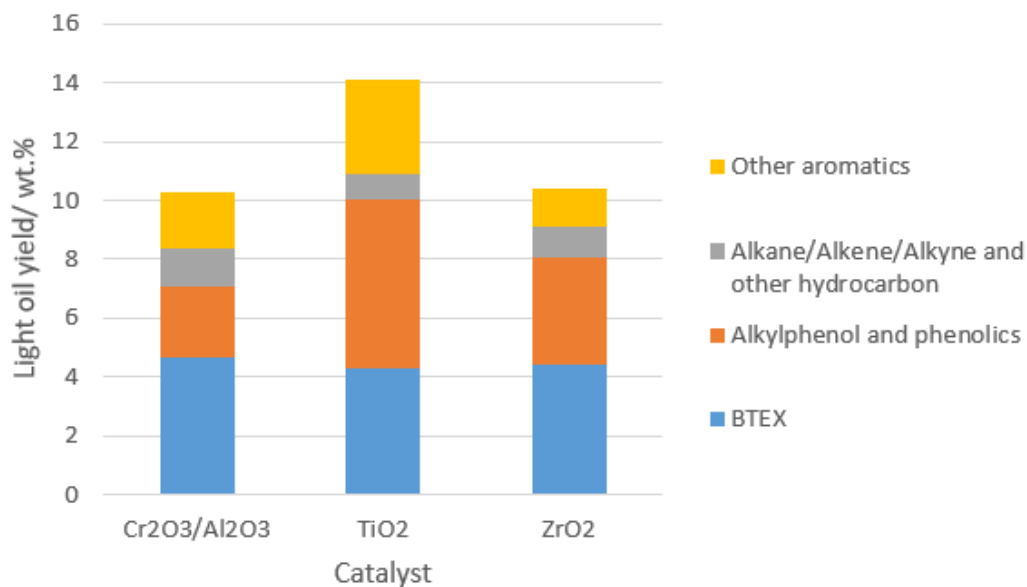
Catalyst	Solid, wt.%	Oil, wt.%	Gas, wt.%	Lignin Conversion, %
Cr ₂ O ₃ /Al ₂ O ₃	57.8	20.1	22.1	81.8
TiO ₂	57.0	29.2	13.8	88.1
ZrO ₂	60.5	25.3	14.2	82.5

The detailed light oil products from runs with Cr₂O₃/Al₂O₃, TiO₂ and ZrO₂ catalysts in lignin

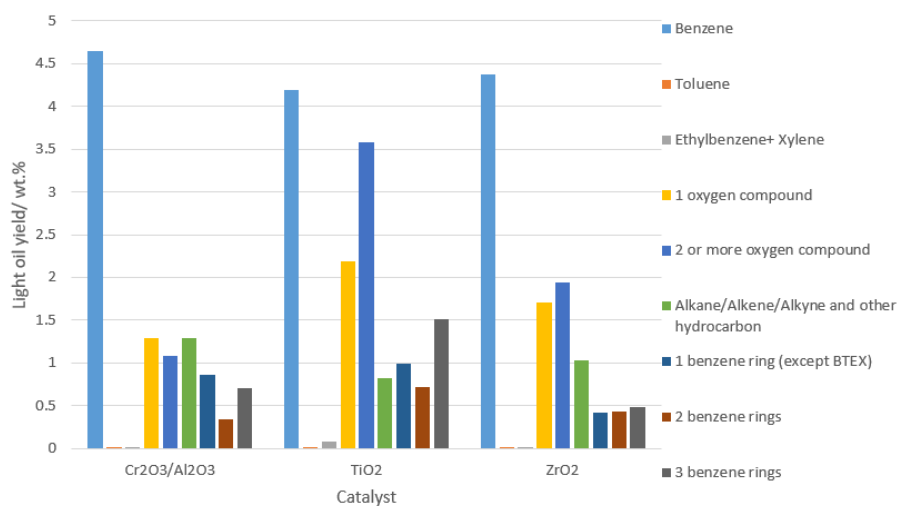
and CH₄ pyrolysis experiments is shown in Figure 6.7. TiO₂ catalyst had the highest light oil yield (14.1 wt.%) among all catalysts illustrated in this chapter. However, the main products of these light oils were alkylphenol and phenols (especially 3.6 wt.% of compounds with two or more oxygens) and other aromatics (which had a high 3.2 wt.% of polyaromatics with three benzene rings). That means TiO₂ catalyst had very limited function on C-O bond breaking and polyaromatics depolymerization. The high light oil yield obtained can be explained by TiO₂ good performance on C-C bond especially the C-C bond between two lignin monomers, which can break large lignin molecules into smaller aromatic molecules. However, it seems that these small polyaromatics and alkylphenols cannot be further cracked effectively.

ZrO₂ catalyst had a similar performance to TiO₂, with high alkylphenol and phenols yield. Although ZrO₂ had much lower surface area, pore volume and average pore diameter than TiO₂, the polyaromatics yield of ZrO₂ catalyst experiment was lower (0.48 wt.% of species with two aromatic rings and 1.3 wt.% with three) than TiO₂ case when the yield of BTEX plus monoaromatics was in a similar level (4.8 wt.% in ZrO₂ vs 5.3 wt.%). That means ZrO₂ tends to generate more monoaromatics or avoid re-polymerization of light molecules when compared with TiO₂.

The Cr₂O₃/Al₂O₃ catalyst experiment produced a BTEX yield of 4.7 wt.% and light oil yield of 10.3 wt.%. The potential way to improve the Cr₂O₃/Al₂O₃ catalyst performance may be by establishing a bimetal catalyst system containing Cr₂O₃/Al₂O₃ and another metal, like Fe in the case illustrated above.



(a)



(b)

Figure 6.7 Light oil yields distribution during pre-oxidated Kraft lignin pyrolysis at 580 °C, 1 bar, 80% CH₄, 1.5:1 sand:pre-treated lignin, 5g catalyst, 1.15 L min⁻¹ flow rate, 1.5 g min⁻¹ feeding rate. (a). group, (b) more detailed disaggregation.

Cr₂O₃/Al₂O₃ catalyst had a better performance on H₂, CO and CO₂ generation when compared with TiO₂ and ZrO₂, and reached a similar level with Ni-only catalysts, which can be obtained from Table 6.11. That means Cr₂O₃/Al₂O₃ catalyst had some ability to crack C-O bond in lignin, but this ability was not as good as the combination of Mo and Ni.

Table 6.11 Outlet gas composition in Cr₂O₃/Al₂O₃, TiO₂, ZrO₂ catalyst experiments (N₂ as background gas)

	Cr ₂ O ₃ /Al ₂ O ₃ (vol.%)	TiO ₂ (vol.%)	ZrO ₂ (vol.%)
H ₂	4.7	1.1	1.9
CO	10.3	8.9	8.6
CO ₂	1.2	0.8	1.1
CH ₄	62.3	67.9	63.1

6.3.5 Performance of In-situ and Ex-situ Catalysts

The two-stage fluidized/fixed bed reactor system illustrated in Chapter 3 was used in experiments described in this section. To figure out the performance in pure CH₄ pyrolysis of the fixed bed reactor used as second stage, two catalytic experiments (one with ex-situ catalyst only and the other with both in-situ and ex-situ) without lignin were carried out with this setup. Subsequently, two experiments with lignin and CH₄ under the same conditions were done in the combined fluidized and fixed beds system (result shown in Table 6.12).

When compared with only in-situ Ni/Al₂O₃-SiO₂ CH₄ only experiments, the ex-situ Ni/Al₂O₃-SiO₂ CH₄ only experiment had lower H₂ and light oil yields (21.2 mol.% and 12.1 wt.% in in-situ catalyst; 20.4 mol.% and 10.8 wt.% in ex-situ catalyst). That means the Ni/Al₂O₃-SiO₂ had a better performance in fluidized bed reactor in DMA reaction. That also explained why the H₂ and light oil yields of 2.5 g in-situ + 2.5 g ex-situ Ni/Al₂O₃-SiO₂ catalyst experiments was lower than 5 g in-situ catalyst experiment but higher than 5 g ex-situ catalyst experiment.

The results of these two-stage system pure CH₄ experiments are shown in Table 6.13. The oil and H₂ yields when the catalyst was used ex-situ in the fixed bed reactor only were lower than in the case shown in Chapter 4 (also in Table 6.13) of in-situ catalyst only. On the other hand, yields were slightly higher in both in-situ and ex-situ catalyst experiment when compared with the result shown in Chapter 4. Thus, two stage reactor with in-situ and ex-situ catalyst was a potential method to provide more H₂ to lignin pyrolysis.

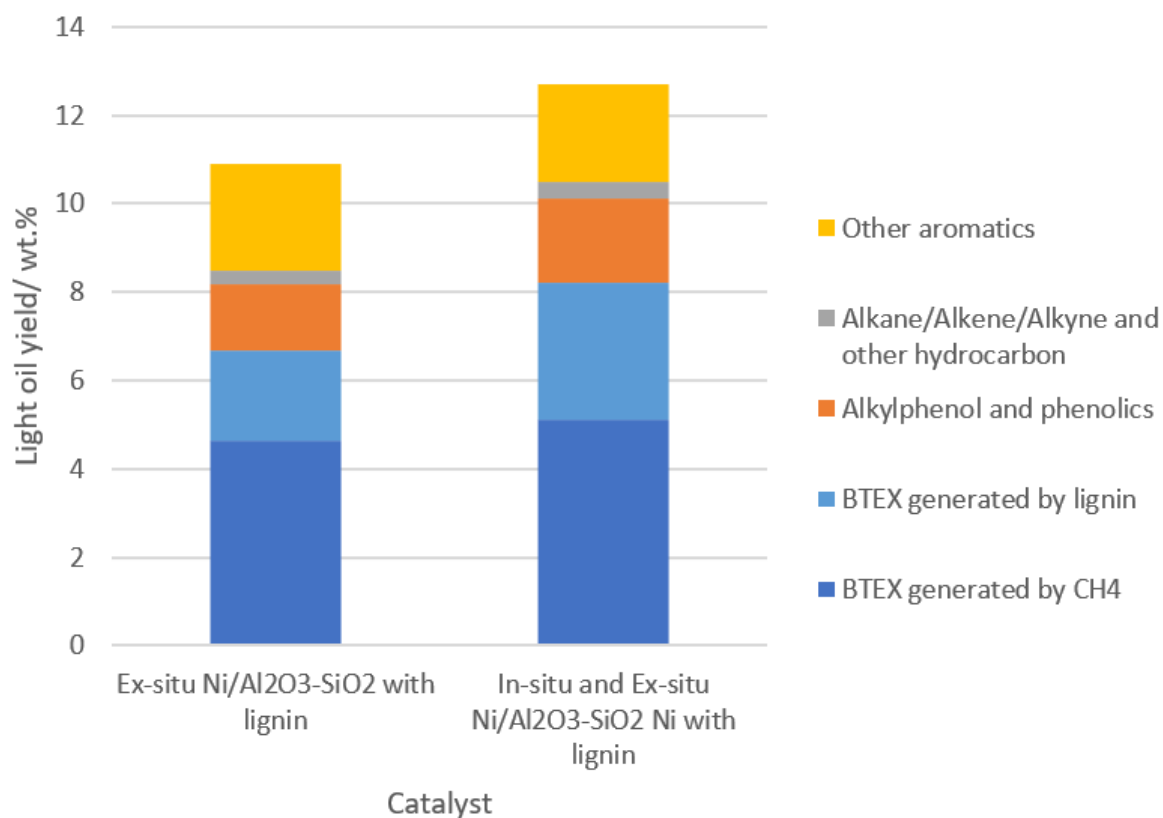
The lignin and CH₄ simultaneous pyrolysis experiment results are shown in Figure 6.8. When compared with the in-situ use of 5 g Ni/Al₂O₃-SiO₂ catalyst experiment (result shown in

Chapter 5), the experiment with ex-situ catalyst only had a slightly lower light oil yield (10.9 wt.%) and lower BTEX yield (6.7% wt). This may point at a better contact between catalyst and reactants in the fluidized bed than in the fixed bed reactor. The in-situ and ex-situ catalyst experiment had a higher light oil yield (12.71 wt.%) than both single in-situ or ex-situ catalyst experiments. The mono-oxygenated alkylphenol and phenols had highest yields in this in-situ and ex-situ catalyst experiment. That proved that lignin can be more completely cracked in the two-stage system than with a single stage only

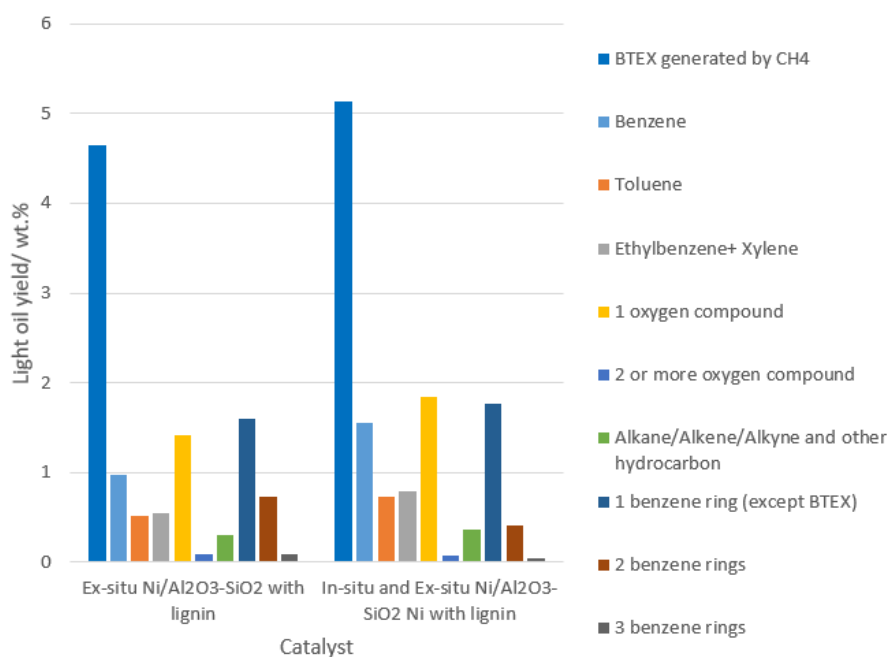
When compared with all other experiments discussed in this chapter, the result of experiment had both in-situ and ex-situ Ni/Al₂O₃-SiO₂ catalyst (Table 6.12) had the highest (92.1%) lignin conversion and the lowest solid yield. This is thought to be due to the following effects. First, according to the result shown in Chapter 5, a decrease in catalyst amount in the fluidized bed reactor only leads to a limited reduction in the lignin conversion (less than 1.5%). Therefore, lignin conversion in fluidized bed may not have experienced a large decrease by only using 2.5 g of catalyst in first stage bed. Second, some unreacted lignin and not completely cracked solid can flow into the fixed bed reactor employed as second stage, providing further residence time for lignin conversion. The result of only ex-situ Ni/Al₂O₃-SiO₂ catalyst experiment led to lower lignin conversion, as well as oil and gas yields than the in-situ only Ni/Al₂O₃-SiO₂ catalyst experiment. That proved the fluidized bed reactor used in this study had a better performance on simultaneous CH₄ and lignin pyrolysis than the fixed bed reactor.

Table 6.12 Products yields and lignin conversion of ex-situ Ni/Al₂O₃-SiO₂, in-situ and ex-situ Ni/Al₂O₃-SiO₂ catalysts with lignin.

Catalyst	Solid, wt.%	Oil, wt.%	Gas, wt.%	Lignin Conversion, %
ex-situ Ni/Al ₂ O ₃ -SiO ₂	52.1	26.4	21.5	85.5
in-situ and ex- situ Ni/Al ₂ O ₃ - SiO ₂ catalysts	41.5	28.7	29.8	92.1



(a)



(b)

Figure 6.8 Light oil yields distribution during pre-oxidated Kraft lignin pyrolysis at 580 °C, 1 bar, 80% CH₄, 1.5:1 sand:pre-treated lignin, 5g catalyst, 1.15 L min⁻¹ flow rate, 1.5 g min⁻¹ feeding rate. (a). group, (b) more detailed disaggregation.

Table 6.13 Yields and selectivity results in different two-stage setup conditions

Temperature, (°C)	Feedstock CH ₄ Concentration (%)	Catalyst and amount	CH ₄ conversion, mol.%	H ₂ yield, mol.%	Oil yield, wt.%	Oil selectivity, wt.%	Weight loss ratio of catalyst samples on TGA, wt.%	Deposit carbon selectivity, wt.%
580	80	5 g, Ex-situ Ni/Al ₂ O ₃ -SiO ₂	31.3	20.4	10.8	57.9	6.2	40.3
		5 g, In-situ Ni/Al ₂ O ₃ -SiO ₂	33.2	21.2	12.1	59.2	5.8	39.4
		2.5 + 2.5 g, In- situ + Ex-situ Ni/Al ₂ O ₃ -SiO ₂	32.9	21.1	11.5	58.4	5.3	37.7

The gas products also need to be mentioned. When compared with the in-situ only Ni/Al₂O₃-SiO₂ catalyst with lignin experiment in Table 6.14, ex-situ Ni/Al₂O₃-SiO₂ with lignin experiment had lower gas concentration which was because in fixed bed reactor, the H₂ concentration generated by DMA reaction was also lower. The in-situ and ex-situ Ni/Al₂O₃-SiO₂ with lignin experiment had a higher gas concentration that was because the ex-situ catalyst can directly involve in further pyrolysis processes based on intermediates from fluidized bed reactor. These intermediates can be further cracked in fixed bed and the bed length was obviously longer in in-situ and ex-situ catalyst experiment than in only in-situ catalyst experiment.

Table 6.14 Outlet gas composition in in-situ and ex-situ catalyst experiments. (N₂ as background gas)

	Ex-situ Ni/Al ₂ O ₃ -SiO ₂ with lignin (vol.%)	In-situ and Ex-situ Ni/Al ₂ O ₃ -SiO ₂ with lignin (vol.%)
H ₂	13.5	17.2
CO	15.4	16.3
CO ₂	3.6	6.1
CH ₄	49.3	44.8

6.3.6 Cross-comparison of All Catalysts

When summarized all results shown above, the total oil yield showed variations with the catalyst employed from the lowest with Ni/Al₂O₃ catalyst to the highest when Ni/Al₂O₃-SiO₂ was used as in-situ and ex-situ catalyst and TiO₂. Although the TiO₂ catalyst experiment had the highest total oil and light oil yield, polyaromatics were obtained in high yield (2.2 wt.%) as well as compounds with two or more oxygen atoms (3.6 wt.%). Thus, the best quality oil was achieved with Ni/Al₂O₃-SiO₂ as in-situ and ex-situ catalyst.

Lignin conversion increased from Ni/Al₂O₃ catalyst to Ni/Al₂O₃-SiO₂ as in-situ and ex-situ catalyst. However, lignin conversion was very close between different catalysts, excepting both in-situ and ex-situ catalyst and Ni/Al₂O₃. The highest 92.1% lignin conversion in Ni/Al₂O₃-SiO₂ as in-situ and ex-situ catalyst was approximately 20% higher than the lowest lignin

conversion in Ni/Al₂O₃. The second highest lignin conversion was obtained with TiO₂ as catalyst (88.1%), which was only less than 10 % higher than that obtained with Ni/ACF. This result showed all catalysts, except Ni/Al₂O₃, had good performances on lignin cracking. And even lowest Ni/Al₂O₃ experiment still has 73.5% lignin conversion rate, which means lignin pyrolysis is predominantly thermally-induced and can operate without good catalyst. When compared with only in-situ Ni/Al₂O₃-SiO₂ catalyst or only ex-situ Ni/Al₂O₃-SiO₂ catalyst experiment, The lignin conversion of both in-situ and ex-situ Ni/Al₂O₃-SiO₂ catalyst experiment increased for more than 6%. This further proves the advantage of combination of in-situ and ex-situ catalyst.

In terms of BTEX, the target products, the lowest yield was obtained with the Ni/Al₂O₃ catalyst (1.3 wt.%), while the highest again resulted from Ni/Al₂O₃-SiO₂ used both as in-situ and ex-situ catalyst (8.2 wt.%). Although high-MoNi/Al₂O₃ did not lead to the highest BTEX yield, it had a good oxygen removal performance. According to the calculations shown in Figure 6.9, the high-MoNi/Al₂O₃ catalyst had the lowest (9.5 wt.%) alkylphenol and phenols to total light oil yield ratio. This made high-MoNi/Al₂O₃ the best catalyst to remove oxygen from lignin. Ni/Al₂O₃, TiO₂ and ZrO₂ catalyst had limited ability to remove oxygen, which led to a relatively high alkylphenol and phenolics concentrations in the light oil. Among these catalysts, TiO₂ showed the highest yield of two or more oxygen compounds, which was much higher than the results of all other catalysts and nearly twice that of the second highest (ZrO₂ with 1.9 wt.%) and the third highest (low-MoNi/Al₂O₃ with 1.4 wt.%). In terms of gas yields, the both in-situ and ex-situ Ni/Al₂O₃-SiO₂ catalyst experiment achieved the highest at 29.8% with high concentrations of H₂, CO and CO₂. This strategy of using two stages also led to the highest H₂ concentration in outlet gas, which can be explained by a longer catalyst bed length in these experiments. That means CH₄ had longer residence time in reaction zone which is important because under 80% CH₄ condition, the CH₄ was not completely converted according to the result shown in Chapter 4. When compared with Ni catalysts (except Ni/Al₂O₃), the H₂ concentration in outlet gas was relatively low in all other catalysts, even including the two Mo-Ni catalysts. The relatively low H₂ concentration in Mo-Ni catalyst experiments may be a consequence of more H₂ being consumed to remove the oxygen from lignin, which is aligned with the high outlet CO and CO₂ concentrations in Mo-Ni catalyst experiments.

The solid yields of these catalysts were in the range of 41.5 wt.% in both in- and ex-situ catalyst experiment to 60.5 wt.% with ZrO_2 . According to previous research the KL and CH_4 simultaneous pyrolysis usually had a solid yield range between 50.0 wt.% (Fe/HZSM-5 as catalyst) to 60.0 wt.% (Mo/HZSM-5 as catalyst).^[129, 140] Thus, the result of solid yield in only in-situ Ni/ Al_2O_3 - SiO_2 catalyst (49.8 wt.%) and both in- and ex-situ Ni/ Al_2O_3 - SiO_2 catalyst (41.5 wt.%) was better than previous research.

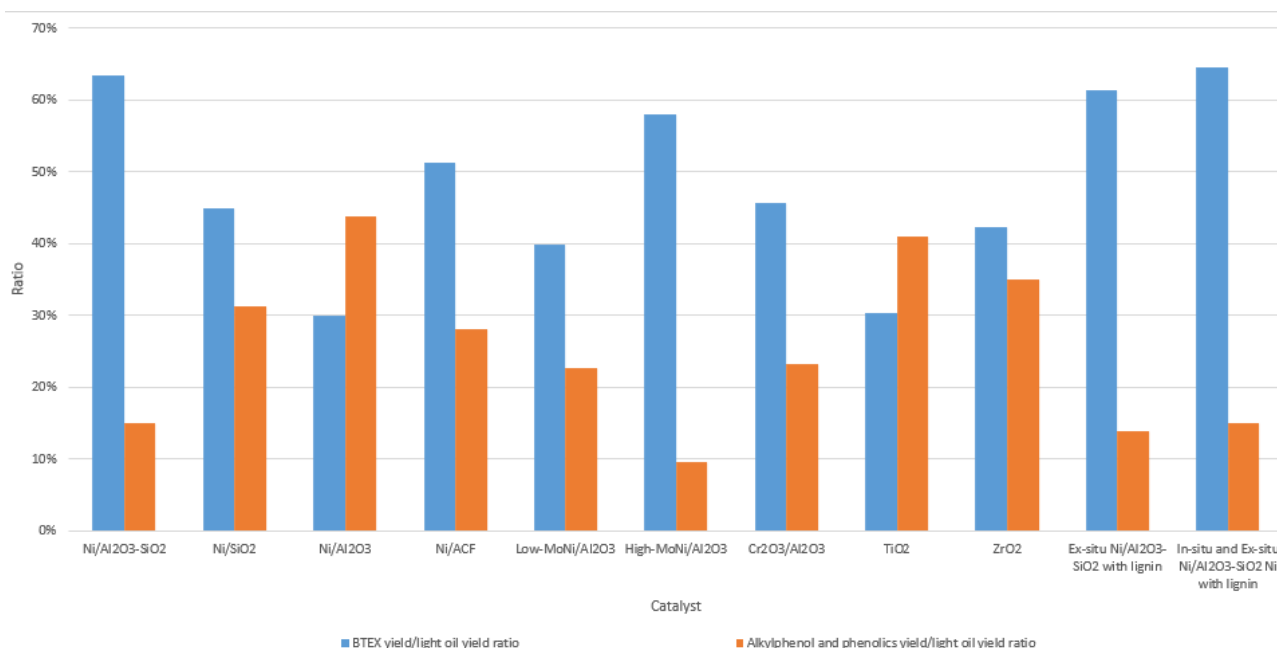


Figure 6.9 BTEX to light oil ratio and alkylphenol and phenols to light oil yield ratio obtained with different catalysts

6.4 Conclusions

The performance of different catalysts on CH_4 and lignin co-pyrolysis has been studied. The Ni/ Al_2O_3 - SiO_2 catalyst as in-situ and ex-situ achieved the highest lignin conversion and second high oil yield. Although TiO_2 had the highest oil yield, the oil produced by it still contained a large amount of oxygen and polyaromatics. Thus, Ni/ Al_2O_3 - SiO_2 catalyst as in-situ and ex-situ catalyst was chosen as the best method to generate target products. Other catalyst combinations on in-situ and ex-situ would be an interesting topic in future work.

The catalyst support can be another interesting topic when the metal concentration was fixed. This study only had limited study on catalyst support and found different support can obviously affect the resulting products.

- (1) Ni/Al₂O₃-SiO₂ catalyst led a much better performance in terms of light oil and gas yields than Ni/SiO₂ catalyst. That was not only because the higher Ni concentration, larger surface area, pore volume and pore size in Ni/Al₂O₃-SiO₂, but also because the Ni/SiO₂ catalyst did not have a good Ni crystal structure based on XRD result shown in Chapter 4.
- (2) Comparison of two experiments done in the same 20% Ni catalyst using Al₂O₃ and ACF as support also showed an obvious difference in light oil yield. The ACF-supported catalyst had a much higher surface area and pore volume than all other catalysts, which may have played a role in its better performance, generating more H₂ and light oil than Al₂O₃ one. However, the density of ACF as support was also lower than all other catalysts and there was a loss of catalysts from the reactor by entrainment in the gas during the experiment. Therefore, less amount of this catalyst was available for the reaction, making it unsuitable for fluidized bed operation. However, it could work better in a fixed bed reactor, which can be a future work direction.
- (3) The Mo-Ni based catalysts showed an interesting phenomenon with low-MoNi/Al₂O₃ having a higher light oil yield than high-MoNi/Al₂O₃ catalyst. However, the high-MoNi/Al₂O₃ had higher yields of BTEX, monoaromatics and gas as well as lignin conversion. This the higher Mo concentration can help in further cracking the intermediate products to smaller molecules. Parts of these intermediate products were even further cracked into gas, making the light oil yield to lower than that of low-MoNi/Al₂O₃ catalyst.
- (4) TiO₂ was another important catalyst employed in this chapter. It reached a high light oil yield. However, the result of TiO₂ based catalyst showed that the BTEX and monoaromatics yields were lower than Ni-based catalyst. The main light oil products of TiO₂ based catalyst experiments were alkylphenol and phenols. This means TiO₂ as catalyst had a bad performance on breaking C-O bond, maybe due to insufficient H₂ being available. ZrO₂ used in this study had unfavorable textural properties, which caused relatively poor results on light oil, gas yield and lignin conversion rate.
- (5) The ex-situ catalyst experiment using fixed bed reactor showed that the Ni/Al₂O₃-SiO₂ had a better performance in fluidized bed than fixed bed reactor. Moreover, the in-situ plus ex-situ catalyst experiment showed that the combination of fluidized and fixed bed reactor can achieve a higher light oil yield. That was because the fixed bed reactor connected behind

the fluidized bed reactor lengthened the bed length and extended the residence time of lignin at high temperatures in the presence of catalyst. The added ex-situ catalyst can also further crack intermediate products generated in a fluidized bed reactor into smaller molecules.

Chapter 7. Conclusions and Recommendations for Future Work

7.1 Summary

DMA and lignin upgrading experiments were carried out in an existing lab-scale continuous spouted fluidized bed reactor which can operate at pressurized atmospheres. Modification of the inner diameter of the spout line was made to allow the reactor to be used with Kraft lignin injection. An existing second stage fixed bed reactor directly linked downstream from the fluidized bed reactor was used to test the performance of Ni/Al₂O₃-SiO₂ as catalyst in in-situ and ex-situ conditions. Quartz wool and wire mesh were used in this fixed bed reactor to hold the catalyst in place.

CH₄-only DMA experiments at temperatures between 550 °C to 700 °C and CH₄ and Kraft lignin simultaneous pyrolysis experiments at 580 °C were successfully run in the modified continuous fluidized bed reactor. In CH₄-only experiments, the influence of CH₄ concentration, catalyst, catalyst weight and temperature were tested. The effect of CH₄ concentration was done under 30% and 80% of total inlet gas concentration with N₂ as balance. Two catalyst weights, 1.56 g and 5 g, were investigated. The effect of temperature was tested in experiments at 550 °C, 600 °C, 650 °C and 700 °C. Catalysts used in CH₄-only experiments included as received and reduced Ni/Al₂O₃-SiO₂, Ni/SiO₂. In these CH₄-only experiments, the yields, CH₄ conversion, selectivity and weight loss ratio of catalyst samples were obtained. The H₂ concentration as a function of time was acquired with the use of an on-line gas analyser. It was shown that under 600 °C, 5 g Ni/Al₂O₃-SiO₂, which had been reduced in the fluidized reactor before the start of the experiment, had a significantly slower deactivation rate. 600 °C was also the best condition for H₂ and oil yields. Using only 1.56 g of catalyst was found unsuitable for the experiment as catalyst losses by entrainment in the gas during fluidized bed experiments adversely affected the results. Ni/Al₂O₃-SiO₂ was found the best catalyst to generate H₂ and oil in CH₄-only experiments.

In CH₄ and lignin simultaneous pyrolysis experiments, the effect of H₂ source, temperature, feeding rate of solid feedstock, catalyst type and amount, gas flow rate, feedstock dilution ratio, pressure and CH₄ concentration were tested. In-situ generated H₂ by CH₄ was proved to lead to

a better oil yield than external H₂ and inert atmosphere (lignin pyrolysis). 600 °C seemed to be the best temperature for oil generation. However, under 600 °C, the experimental operation was hard to keep under a safe condition, and 580 °C was chosen as the optimal instead. The feeding rate of solid feedstock did not have an obvious effect on oil generation, but when it became too large, the oil yield can decrease as heavy oil generated by lignin pyrolysis could deposit at the bottom of the fluidized bed reactor (below the spout injection point) and cannot be carried away by the gas. The effect of catalyst weight was tested by using 3.5 g and 5 g separately. Based on the results from CH₄-only experiments, the low-level catalyst amount was chosen as 3.5 g (more than double the 1.56 g used in those experiments). Gas flow rate was found to be an important variable affecting oil and gas yields as it determines fluidization conditions as well as the residence time of volatiles in the bed. Low gas flow rate allowed more lignin and volatile to undergo greater extents of cracking before leaving the bed. Feedstock dilution ratio did not affect the oil yield significantly, thus a dilution ratio that did not require too much sand of particle size less than 150 μm (which was hard to obtain) was chosen as the optimal condition. High pressure can reduce the DMA reaction, which provide H₂ for lignin pyrolysis and oil, further reducing the total oil yield. High CH₄ concentration increased H₂ and oil production, increasing the target product yields. An experiment with TiO₂ as catalyst had the highest total oil yield but not that of light oil. Ni/Al₂O₃-SiO₂ catalyst used as in-situ and ex-situ catalyst in the two-stage system led to the highest lignin conversion and light oil yield.

7.2 Conclusions

The main conclusions of this project are:

- (1) **DMA reaction:** It was observed that CH₄ only experiment in fluidized bed reactor can obtain promising products yield under 580 °C (21.2 mol% H₂ yield and 12.1 wt.% oil yield) and 600 °C (29.7 mol% H₂ yield and 16.9 wt.% oil yield) with 5 g Ni/Al₂O₃-SiO₂ catalyst and 80% CH₄ inlet concentration. Experiments with two other catalysts (HZSM-5 and Ni/SiO₂) and no catalyst were also done, and all of them had low products yield. The main reasons causing 5 g Ni/Al₂O₃-SiO₂ catalyst at 580/600 °C to be chosen as the optimal condition for H₂ and oil generation are discussed below. First, the H₂ fed during catalyst

reduction process can be stored by Ni/Al₂O₃-SiO₂ catalyst before CH₄ was injected into and partially guide the carbon to generate nanofiber structures (proved by BET result). This carbon nanofiber could grow in a direction away from the surface of catalyst and not fully cover it, reducing the deactivation rate and generating a high product yield. Secondly, the Ni/Al₂O₃-SiO₂ catalyst has a high active metal concentration, clear crystal structure and good textual properties. The amount of catalyst used in these experiments should be large enough to avoid the loss of catalyst (carried away from the reactor by the gas) to significantly affect the results. Third, the catalyst deactivation rate was very fast at higher temperature (650 °C and 700 °C), even if the generated H₂ concentration was much higher than at 580 °C and 600 °C at beginning of the CH₄ injection. BET analysis of catalyst from the 700 °C experiment showed that the carbon deposit was mainly in particle shape rather than nanofibers. In conclusion, the most important factors that can improve the H₂ and oil yield in addition to temperature are catalyst activity, resistance to deactivation and amount.

- (2) **CH₄ and KL simultaneous pyrolysis:** Following pure CH₄ experiments, KL was added into the reactor through an adapted solid feeding system. Due to the limitations caused by feedstock agglomeration, pre-oxidated lignin was mixed with sea sand (particle size <150 μm) as the feedstock. To ensure this mixture can be successfully fed into reactor, the total inlet gas flow rate should be higher than the terminal velocity of sea sand (which has a larger density than KL). According to the results illustrated in chapter 5, the most important variables that can affect the oil yield and composition were source of H₂, total inlet gas flow rate, pressure and CH₄ concentration. The detail discussion for these variables is illustrated: (I) The H₂ generated in-situ from CH₄ had several advantages. First, it is produced concurrently with oil products; secondly, the in-situ H₂ is generated on the catalyst surface and therefore directly available for the lignin upgrading reaction. The disadvantage of in-situ H₂ is that it can only generate up to 40% H₂ concentration, even under 80% CH₄ concentration experiment, which means this in-situ H₂ generation strategy cannot provide very high H₂ concentrations. (II) Because of the high total inlet gas flow rate required by feeding system, some unreacted or not fully reacted small particle size KL and volatiles can be carried out from the reactor. A high inlet gas flow rate reduces the

residence time of volatiles in the reactor, which prevents heavy volatiles to be further cracked into light oil. Thus, when the total gas flow rate decreased from 2 L min⁻¹ to 1.15 L min⁻¹, all total oil yield, gas yield and light oil yield increased obviously. Another way to further extend the residence time was lengthening the bed by acquiring a longer quartz liner and using more bed material in the fluidized bed or connect the fluidized bed reactor with another fixed/fluidized bed reactor. (III) pressure can inhibit the CH₄ conversion into H₂ and oil, but it can also aid in lignin hydrocracking and hydrodeoxygenation. A balance should be found in this in-situ H₂ generation in lignin pyrolysis experiment to generate enough H₂ to obtain good BTEX yields. The best experiment pressure was found at 1 bar, as higher pressure (3 bar and 5 bar) significantly reduced the BTEX generated from CH₄, which finally reduced the light oil yield. (IV) The inlet gas CH₄ concentration directly affected the concentration of generated H₂. The 80% CH₄ catalytic experiment led to higher oil yield and lignin conversion than 30% CH₄. Temperature variations between 560 °C and 620 °C, feeding rate, feedstock dilution rate and relatively lower catalyst amounts had minor effects on the oil products yield.

- (3) **Different catalysts in simultaneous pyrolysis:** Four Ni catalysts (Ni/Al₂O₃-SiO₂, Ni/SiO₂, Ni/Al₂O₃, Ni/ACF), two Mo-Ni catalyst and Cr₂O₃, TiO₂, ZrO₂ catalyst were tested to find their advantages and disadvantages. The most interesting results can be summarized as: (I) high Ni concentration catalysts (Ni/Al₂O₃-SiO₂ and Ni/SiO₂) had better performance on oil generation and lignin conversion than low Ni concentration catalysts. (II) the catalyst with ACF as support had extremely higher surface area than all other catalysts but it had a very low density, which led to entrainment and loss of catalyst. Thus, the ACF-supported catalyst is more suitable for fixed bed than fluidized bed reactor. (III) when compared with the Ni catalysts experiment, Mo-Ni catalysts had a better performance on deoxygenation, but lower total oil yield than the Ni/Al₂O₃-SiO₂ catalyst experiment. (IV) The TiO₂ catalyst reached the highest total oil yield and light oil yield among all used catalysts. However, the main compounds in the oil generated in TiO₂ catalyst experiments were alkylphenols, phenolics, polyaromatics. The monoaromatics only have very limited concentration, even in light oil. It is speculated that this might be due to the TiO₂ absorbing H₂ at high temperatures. The best lignin conversion was obtained in both in- and ex-situ Ni/Al₂O₃-

SiO₂ catalyst experiment. That was because ex-situ catalyst bed lengthened the bed and reaction time of lignin and volatiles. Residence time was proved a significant value which affects oil yield and composition. The added ex-situ catalyst can also further crack the intermediate products generated in fluidized bed reactor into smaller molecules. Thus, the performance of other catalysts in in- and ex-situ reactor experiments and the cross combination between them is worth to be studied in future work.

7.3 Recommendations for Future Work

Based on the studies performed in this project, the following areas are suggested for future research.

- (1) In this work, the H₂ concentration generated by CH₄ was still at a relatively low level. That was because the Ni catalyst cannot work for a time long enough at high temperature, which is caused by deposit carbon. Based on thermodynamic equilibrium analysis, CH₄ tends to generate more H₂ at higher temperatures. Thus, some other catalysts need to be tested to improve the H₂ generation performance.
- (2) A kinetic model for lignin or lignin model compounds could be an interesting work to do. It will be beneficial to further understand the participant reactions.
- (3) The feeding system should be further improved for pyrolysis at higher temperature and longer experiment time. Current simultaneous pyrolysis experiments were only done at temperatures lower than 620 °C and experiment times less than 1 h. After upgrading the reactor system, the experiments operated at higher temperatures and longer times are a good point to study. The oil collection parts and processes are another part worth improving. In the current vertical tar trap, the process of disassembling plus evaporating the tar can produce light oil losses.
- (4) The feeding system can be involved in the reduction process and using H₂ in catalyst reduction to remove part of oxygen in lignin added during pre-oxidation. That will not only save the energy, but also reduce the oxygen content in oil yield.
- (5) The recovery of catalyst from the bed material after experiment can represent an important future work direction. The spent catalysts from this study had a similar particle size and

solubility (in both water or chloroform) to the bed material. A method needs to be developed to recover the spent catalyst, so that experiments can be run with the recovered catalyst.

- (6) The combination of in- and ex-situ catalyst pyrolysis was a promising aspect that needs to be discussed. In this study, the in- and ex-situ reactor used the same catalyst. However, the main compounds in the first stage fluidized bed reactor are heavy molecules and in the second stage fixed bed reactor are lighter, having undergone a greater extent of reaction. Thus, using different catalysts in two reactors could be a method to improve the yield of high added-value products. The two-stage reactors system can also use two different temperature aims to the reactants. Because the volatile and intermediate reactants in first stage reactor are different with the reactants in the second stage reactor. The optimal temperature condition of them is different.

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Appendices

Appendix 1 Calculation of Fluidized Bed Incoloy Reactor Reliability

The main reliability analysis for fluidized bed Incoloy reactor was its wall thickness, which has been discussed in Chapter 3. High Pressure Safety Code ^[144] and BSI PD 5500 ^[145] was used to calculate the minimal wall thickness of the Incolloy tube used in this study. The equation is shown in Equation A.1

$$e = \frac{pD_i}{2f-p} \quad \text{Equation A.1}$$

In which, p is the designed operation pressure, D_i is the internal diameter and f is the creep strength.

The creep strength of the Incoloy Alloy 800 HT used in this study was provided by Incoloy company, which is shown in Figure A.1.

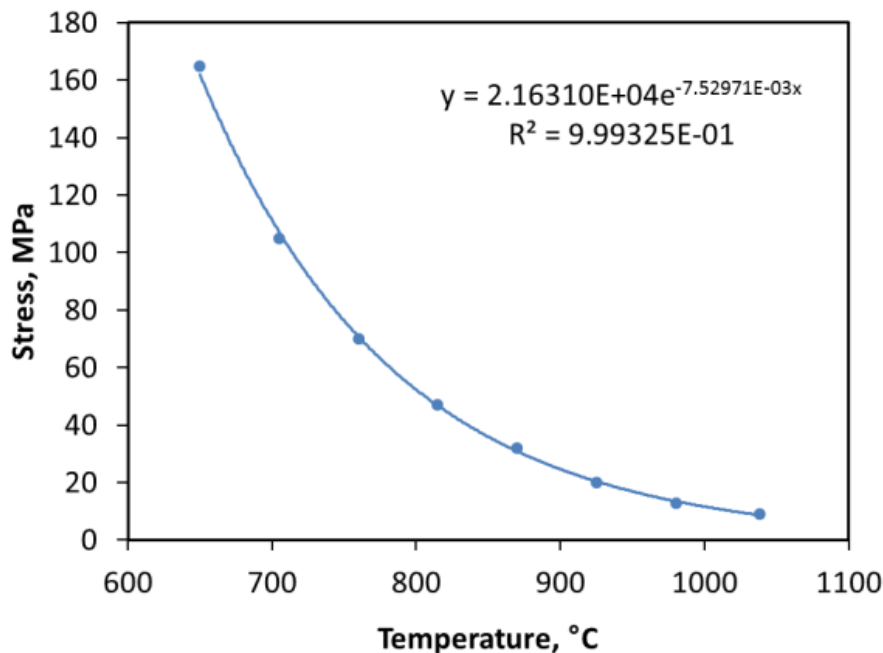


Figure A.1 The creep strength for 1000 h of Incoloy Alloy 800HT (provided by Incolony, 1986)^[146]

As was illustrated in Chapter 3, the minimal wall thickness against the design pressure at both 1000 °C and 1050 °C are shown in Figure A.2.

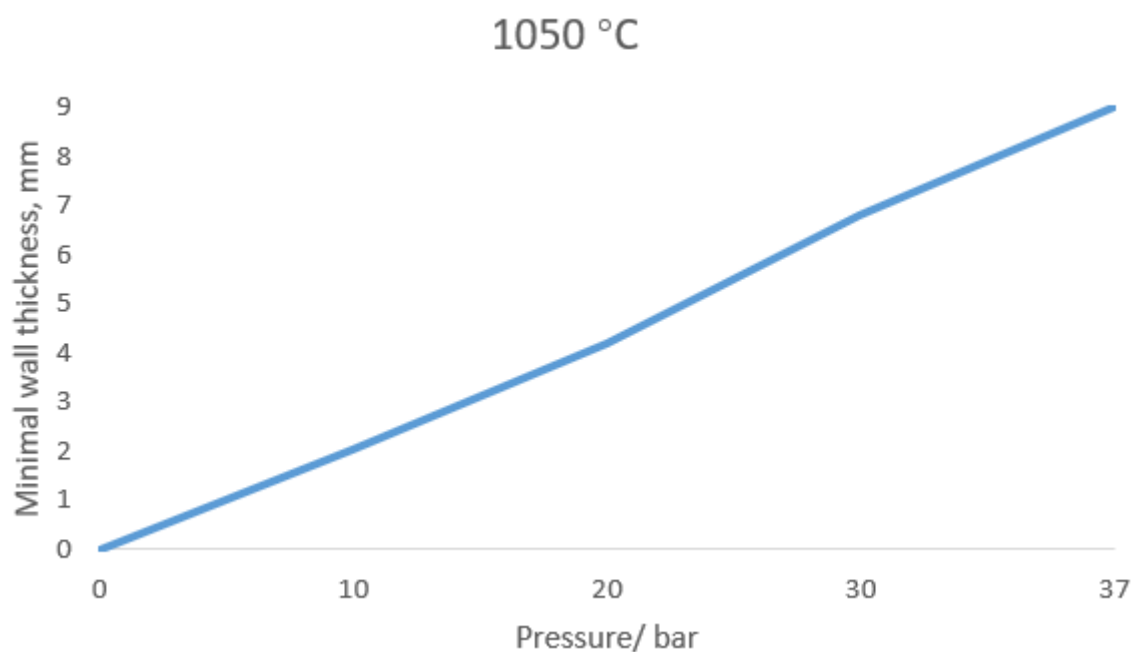
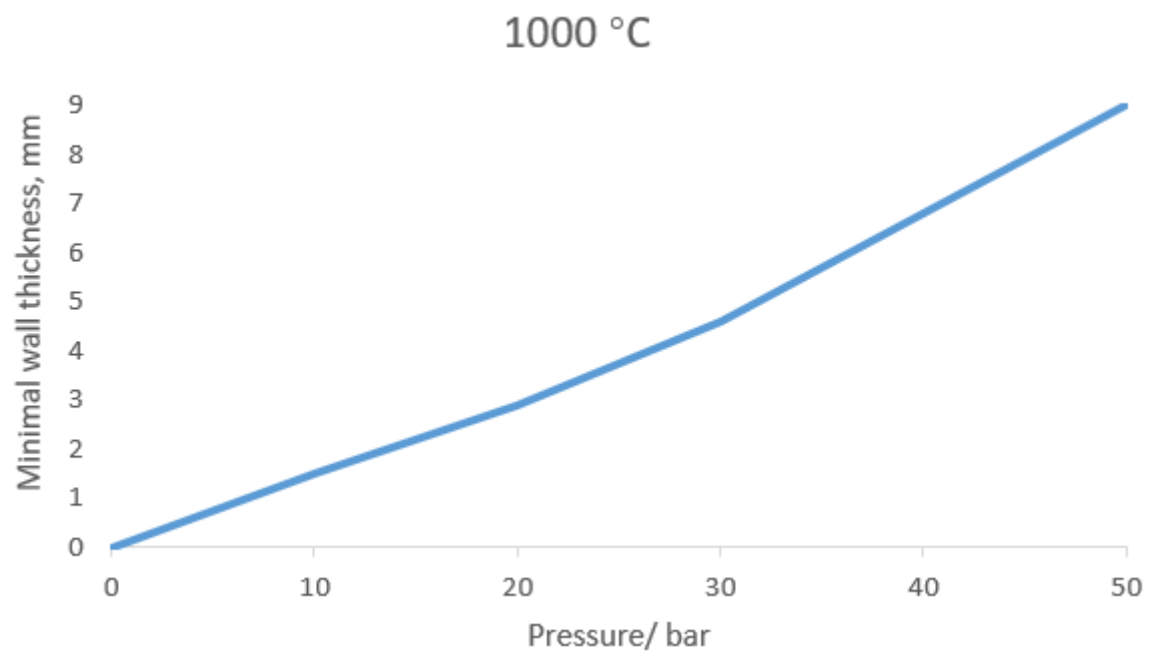


Figure A.2 Required minimum wall thickness for design pressure for 1000 h. (a.1000 °C, b. 1050 °C)

Appendix 2 Solid Feeding System Calculation

As was illustrated in Chapter 3, the DC motor was used to control the feeding rate of solid feeder. This DC motor linked with a 0 to 15 V variable transformer. The feeding rate was adjusted by control the output voltage of this transformer. The calibration of the relationship between voltage of transformer and feeding rate was done by following processes. First, 15 g kraft lignin was weighed by balance and filled into the feedstock hopper. Then, a required output voltage was set for transformer. The time before all kraft lignin dropped out from the hopper was recorded. The feeding rate against voltage can then be calculated with this time data. These steps were done for three times in every voltage test, and the average value was taken. The feeding rate (F_{solid} , g min^{-1}) calibration equation is given in Equation A.2. The relationship between feeding rate and voltage is shown in Figure A.3.

$$F_{solid} = \frac{W_{solid}}{\Delta t} \quad \text{Equation A.2.}$$

Where W_{solid} (g) is the weight of the lignin filled into the hopper, and Δt (min) is the time interval.

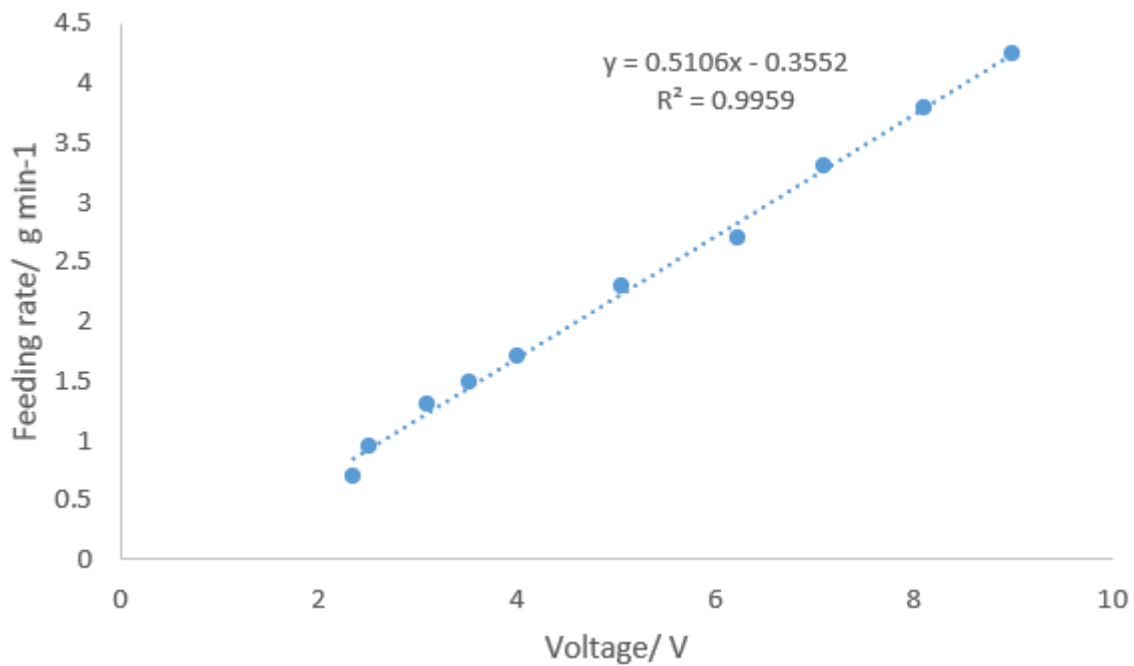
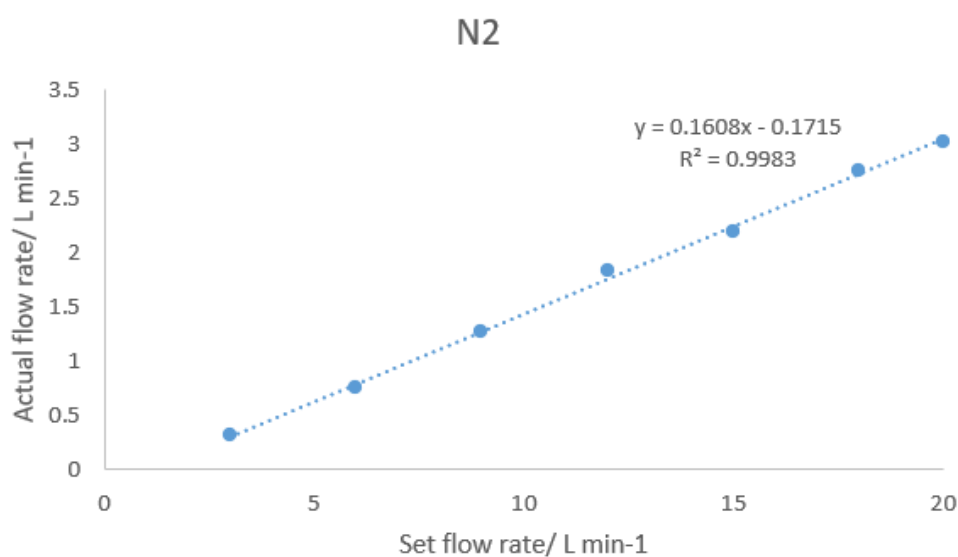


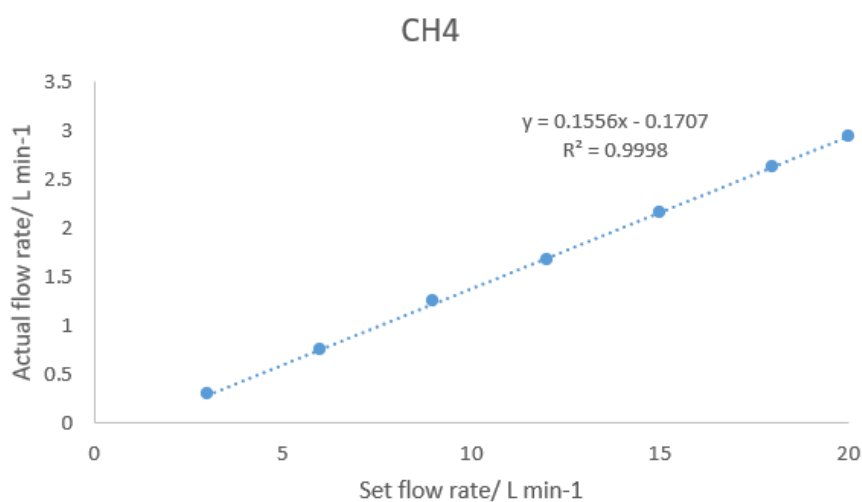
Figure A.3 Calibration of feeding rate

Appendix 3 Calibration of the Mass Flow Controller

The mass flow controller for N₂ and CH₄ was calibrated by a 2000 mL bubble meter. The squeeze bulb which was filled by soap solution set as the bottom of this bubble meter. And on the squeeze bulb, a calibrated glass tube was fixed. The method using this bubble meter to calibrate the mass flow controller was illustrated in previous study ^[147]. The cylinder pressure used in calibration was 10 bar for CH₄ and 5 bar for N₂. Three times repeat tests were done for each flow rate and chosen average value as the final calibration result. The calibration curve of N₂ and CH₄ is shown in Figure A.4.



(a)



(b)

Figure A.4 Calibration of the mass controller (a. N₂, b. CH₄)

Appendix 4 Dry Gas Meter Calibration

N₂ stream was passed to calibrate the dry gas meter with different known flow rate from mass controller calibrated in Appendix 3. The flow rate from the gas meter was calculated by taking the gas volume readings between the time interval (1 min in this tests). The difference between these two reading is the volumetric flow rate measured by gas meter. Each set flow rate was repeat measured for three times and the average value was used as the calibration result. The dry gas meter calibration curve was shown in Figure A.5.

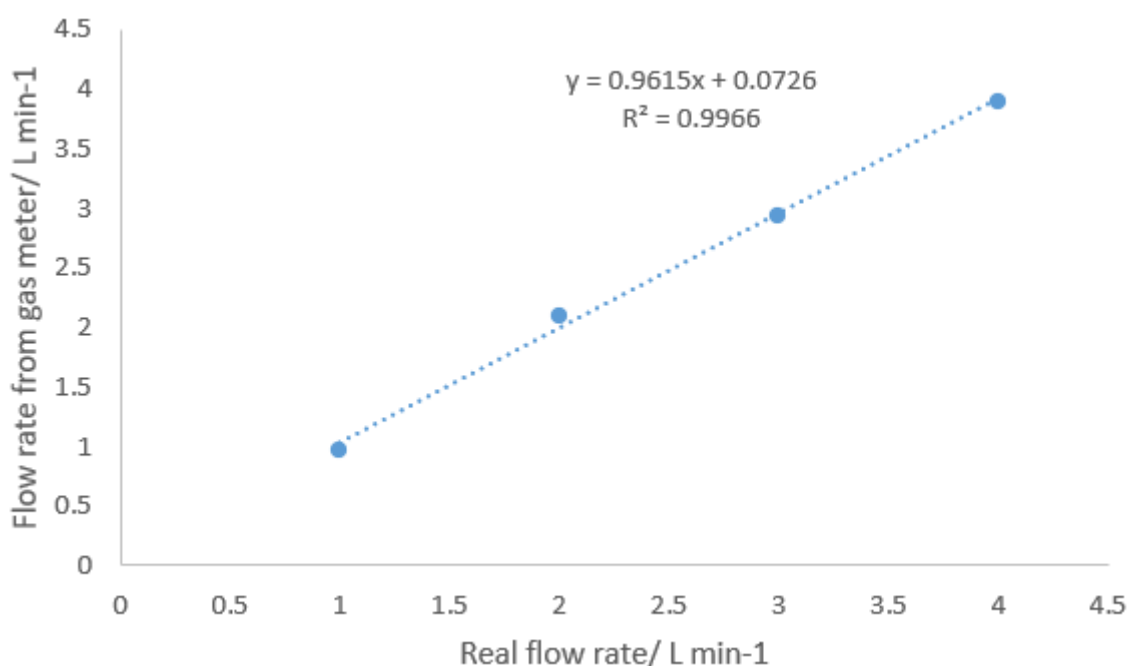


Figure A.5 Calibration of the dry gas meter

Appendix 5 Detail XRF Result of All Catalysts Used in Experiments

Table A.1 The detail elemental concentration of all catalysts used in experiments.

Catalyst	Ni/Al ₂ O ₃ -SiO ₂ (%)	Ni/SiO ₂ (%)	High- MoNi/Al ₂ O ₃ (%)	Cr ₂ O ₃ /Al ₂ O ₃ (%)	Low- MoNi/Al ₂ O ₃ (%)	TiO ₂	ZrO ₂
Mg	0.367	0.269	0.126	0.217	0.118	-	-
Al	4.638	1.454	47.164	65.427	72.917	-	1.122
Si	8.022	28.615	0.615	0.239	-	-	-
P	0.236	0.28	5.025	-	0.375	-	-
Cr	-	-	-	33.496	-	0.132	-
Cl	0.15	0.117	0.153	-	0.158	-	-
Ca	4.818	0.727	0.113	-	0.365	0.123	-
Ti	-	-	-	-	-	98.181	0.2
Fe	0.896	0.794	-	0.209	-	0.151	-
Ni	80.535	66.781	7.851	-	7.236	-	-
Mo	-	-	38.552	-	18.554	-	-
Zr	-	-	-	-	-	0.163	96.078
Hf	-	-	-	-	-	-	2.371

Appendix 6 Calibration for Response Factor of Solvent Chloroform

As was illustrated in Chapter 3, the chloroform as solvent cannot be fully removed during oil collection process to avoid light oil losing. Thus, many chloroform can be detected during GC-MS&FID analyzing. To ensure the accuracy of oil yield, the concentration of chloroform in solvent and oil mixture should be figure out.

The method to figure out the relationship between the chloroform concentration and the chloroform peak area on GC-FID was illustrated below. The chloroform used as solvent was first weighted for the same amount, and then it will be mixed with pure glycerol with different weight ratio. These known concentrations chloroform and glycerol mixture were analyzed by GC-MS&FID, and the chloroform peak was appeared at cutting off time. The relationship between chloroform concentration and its peak area was recorded and is shown in Figure A.6.

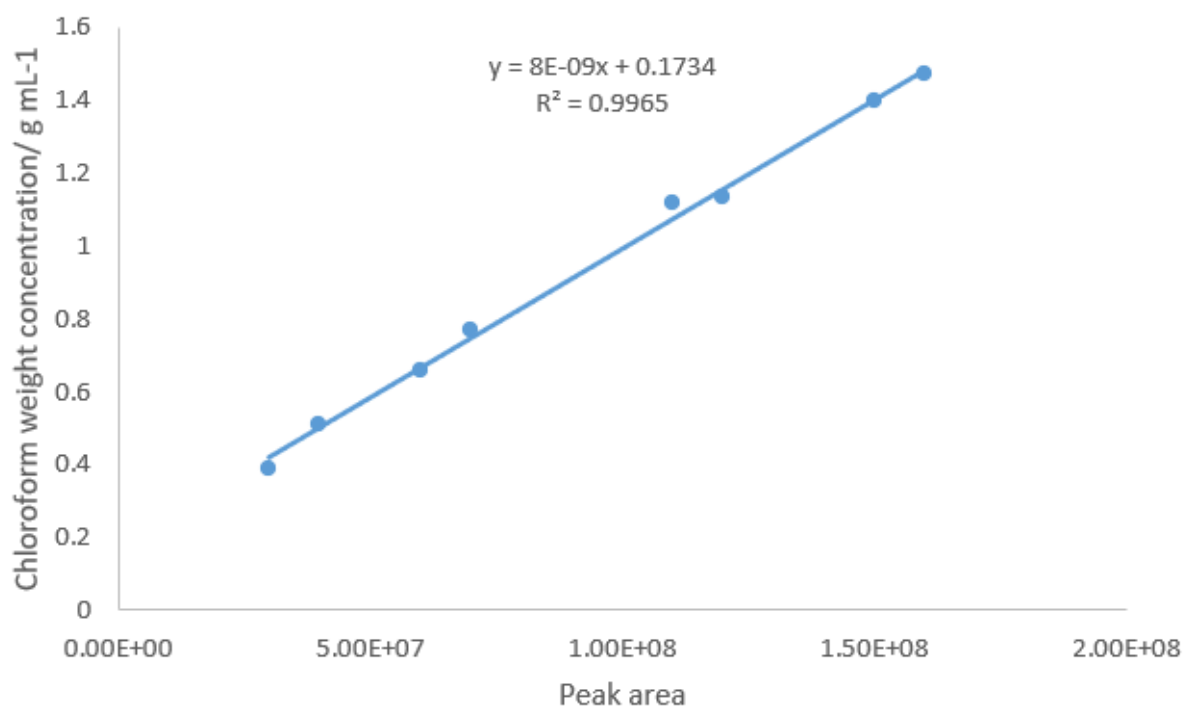


Figure A.6 Calibration of relationship of chloroform weight concentration and peak area