

Electronic Supplementary Information

1 REFINERY OPERATIONS

Crude oil is processed in a refinery to generate valuable smaller carbon-chain species through different processes. Initially, atmospheric distillation is used to separate the oil into various fractions (i.e., naphtha, kerosene, light gas oil, heavy gas oil, long residue) based on their different boiling points. This process requires heat input to achieve the desired separation temperatures. Following which, the long residue is converted in a vacuum distillation process to produce vacuum gas oil (input into the catalytic conversion processes) and vacuum residue (input to the de-coking processes).

The outputs from the distillation units undergo thermal cracking to reduce the length of the carbon chains and, consequently, reduce the viscosity of the residue to produce fuel oil and other products. The fluid catalytic cracker is important as it converts atmospheric gas oil, vacuum gas oil, etc., to produce gasoline, light fuel oils, and fuel gas streams. This process is catalytically driven, and the catalyst is regenerated by burning the coke deposits formed as part of the cracking reactions, releasing unavoidable CO₂ emissions.

A series of processes follow the thermal and catalytic converters as follows:

- Hydrotreating – H₂ is used to reduce impurities such as sulphur, nitrogen, and oxygen in the feedstock.
- Naphtha splitting – hydrotreated naphtha is split into light and heavy naphtha for subsequent processing in the isomerization unit and the catalytic reformer.
- Catalytic reforming – the octane number in naphtha is increased by increasing the aromatics content to produce high-octane liquid, along with H₂, light gases and liquified petroleum gas.

H₂ is also produced as a by-product of the catalytic reforming process and often recovered from the fuel gas streams using a pressure swing adsorption unit. Larger refineries are unable to meet their H₂ requirements purely from by-product generation and usually have dedicated H₂ production plants. Steam methane reforming (SMR) is most commonly used to produce the H₂ feedstock necessary for all the processes (e.g., hydrocracking, hydrotreating, etc.).

1.1 Case study system boundary

The case study considered in this paper relates to a high conversion refinery with a crude capacity of 220,000 barrels per stream day (BPSD) (IEAGHG, 2017). It is representative of a typical European refinery with multiple units running in parallel, offering good flexibility of operation to multiple feedstocks. The refinery uses fuel gases, fuel oils, and coke as the main fuel supplies. Both the crude and vacuum distillation units run entirely on fuel oil. The fluid catalytic cracking unit is the only unit which combusts the coke deposits for energy, and the rest of the refinery uses fuel gases. The SMR unit has a H₂ production capacity of 35,000 Nm³/h and the power plant units have a design capacity of 78 MW. The emission flowrates are tabulated in Table S1.

2 SUPPLEMENTARY DATA

- Where required, an exchange rate of 1€ = 1.188 US\$, and 1£ = 1.386 US\$ is used in the paper.
- The emission data used to generate Figure 1B, and to undertake the CO₂ avoided calculations on, are based on Case 3 from IEAGHG (2017). These emission sources are summarized in Table S1 for completeness.

Table S1. Point sources of emissions in the example refinery case used in this work, from IEAGHG (2017).

Unit code	Unit label	Unit description	Design capacity [BPSD]	y_{CO_2} [% _{vol}]	CO ₂ emissions [t·hr ⁻¹]
0100A	CDU	Crude distillation unit	100,000	11	23.630
0100B			120,000	11	28.634
0300A	NHT	Naphtha hydrotreater	23,000	8	0.834
0300B			27,000		
0350A	NSU	Naphtha splitting unit	23,000	8	1.112
0350B			27,000		
0500A	CRF	Catalytic reforming	15,000	8	10.008
0500B			18,000		
0600A	KHT	Kero HDS	14,000	8	0.556
0600B			12,000		0.278
0700A	HDS	Gasoil HDS	26,000	8	3.336
0700B			39,000		4.448
0800	VHT	Vacuum gasoil treater	50,000	8	7.784
1000	FCC	Fluid catalytic cracker	60,000	17	53.098
1100A	VDU	Vacuum distillation unit	35,000	11	3.892
1100B			51,000		5.838
1200	SMR	Steam methane reformer	-	8	5.838
		Steam methane reformer feed	-	24	25.576
1400	DCU	Delayed coking unit	35,000	8	11.954
2500A	POW	Power plant (NGCC)	-	3	25.020
2500B		Power plant (NG boiler)	-	8	54.210

3 AVOIDED CO₂ CALCULATION

The system boundary for the avoided CO₂ calculation accounts for all the direct emissions released in the refinery. Importantly, it does not address scope 2 and 3 emissions of the refinery. Furthermore, the assessments explicitly consider the quantity of scope 1 and 2 emissions generated by tackling the direct emissions from the refinery. For example, the use of natural gas in a post-combustion CO₂ capture facility could create additional direct (i.e., scope 1 emissions) and indirect (i.e., scope 2 emissions). Similarly, fuel switching with hydrogen or electricity will eliminate scope 1 emissions, but introduce additional scope 2 emissions. Thus, the calculations identify the overall CO₂ avoidance in a refinery following the implementation of a carbon abatement measure – see section 3.1 for more details of the mathematical definition of the CO₂ avoidance rate.

In Figure 2, the avoided CO₂ emissions of the reference plant are calculated as a function of: CO₂ capture rate (CR), fuel direct emissions intensity (DEI), and fuel scope 2 emissions intensity (IEI).

In order to determine the amount of fuel required by the CHP plant to run the capture plant, the total thermal and electrical energy requirements are required. The energy required to implement CO₂ capture on the CHP flue gas is also included in this calculation. It is assumed that the CO₂ concentration of the flue gas from the CHP plant is 8%_{vol}. It is also assumed that the CHP is a steam turbine type and that it can be designed to provide the required split of thermal and electrical energy. Therefore, we are only concerned with the total amount of fuel input required to produce the corresponding amount of energy. A thermal efficiency (η_{th}) of 80% and an electrical efficiency (η_{el}) of 35% are applied (Darrow et al., 2017).

A published model (Danaci et al., 2021) is used to determine the thermal (\hat{E}_{th}) and electrical energy requirements of an MEA-based amine-absorption process for each flue gas stream in Table S1 as well

as the CHP plant. The thermal energy requirement includes the reboiler duty, and the electrical energy requirements include the feed blower and pumps.

The electrical energy requirements for CO₂ product compression are estimated using ASPEN HYSYS using the PRSV fluid package. The CO₂ product from the capture model is delivered under consistent conditions; therefore, this is not required to be undertaken for each scenario. A multi-stage compression with inter-cooling process is assumed (Figure S1) for producing the CO₂ stream at 100 bar_a. The feed temperature to each stage after inter-cooling is 35 °C. The CO₂ from the capture plant is provided at 2.12 bar_a and 35 °C. The resulting electrical energy consumption is estimated at 0.3036 GJ_{el}·t_{CO₂}⁻¹. Then the total electrical energy requirement (\hat{E}_{el}) is the sum of the electrical energy of the capture plant and of the CO₂ product compression.

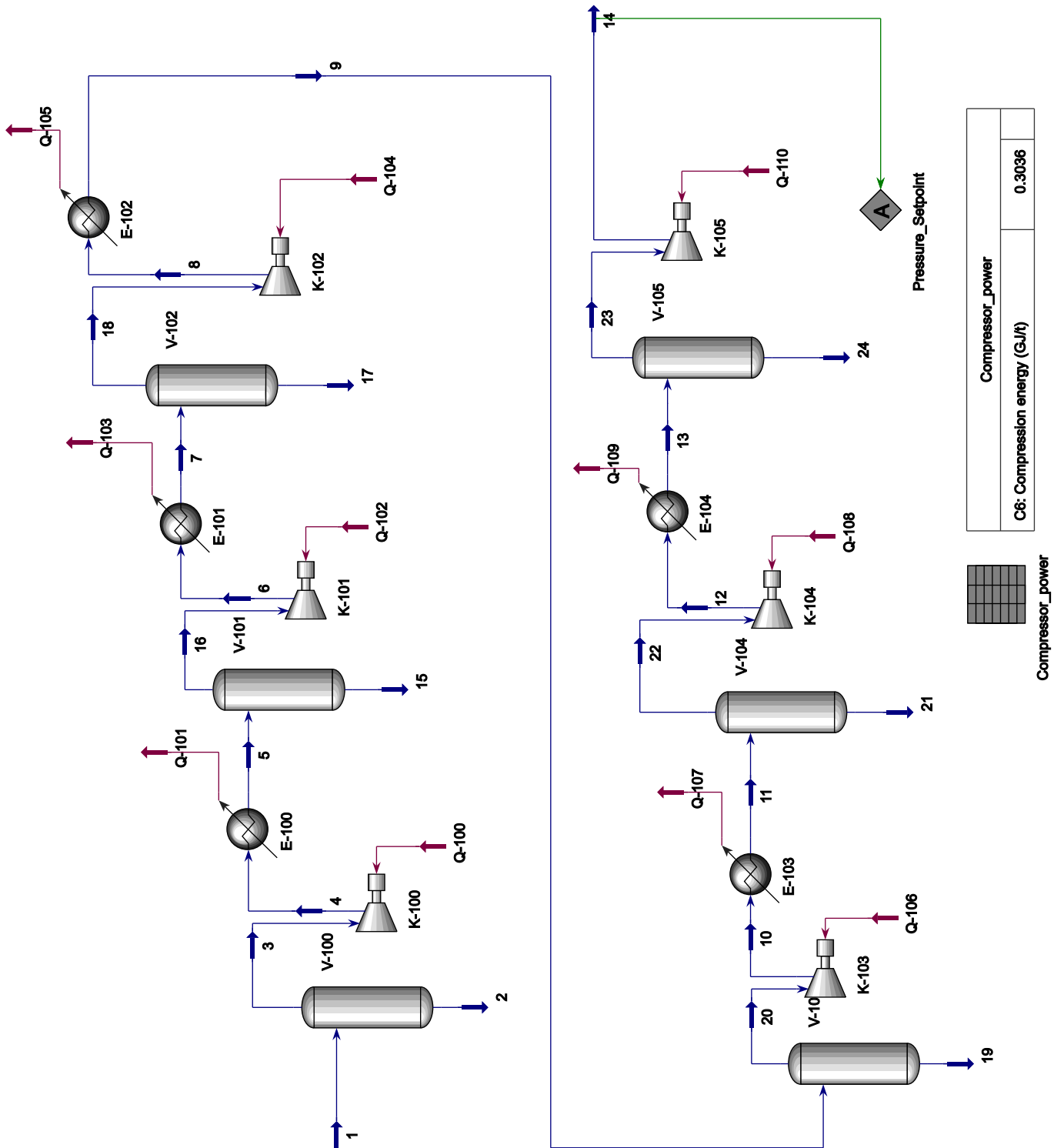


Figure S1. HYSYS flowsheet of CO₂ product compression.

3.1 Method

- The total thermal and electrical energy requirements for CO₂ from the refinery point sources are determined first:

$$E_{\text{th}}^{\text{ref}} = \sum_i^{\text{sources}} CR \times \dot{m}_{\text{CO}_2,i} \times \hat{E}_{\text{th},i} \quad (\text{S1})$$

$$E_{\text{el}}^{\text{ref}} = \sum_i^{\text{sources}} CR \times \dot{m}_{\text{CO}_2,i} \times \hat{E}_{\text{el},i} \quad (\text{S2})$$

- The residual emissions from the refinery point sources can be calculated next:

$$RE^{\text{ref}} = \sum_i^{\text{sources}} (1 - CR) \times \dot{m}_{\text{CO}_2,i} \quad (\text{S3})$$

- Then, the CO₂ emissions from the CHP plant (Ω) can be determined from the following system of equations:

$$E_{\text{th}}^{\text{tot}} = E_{\text{th}}^{\text{ref}} + E_{\text{th}}^{\text{CHP}} = E_{\text{th}}^{\text{ref}} + CR \times \Omega \times \hat{E}_{\text{th}}^{\text{CHP}} \quad (\text{S4})$$

$$E_{\text{el}}^{\text{tot}} = E_{\text{el}}^{\text{ref}} + E_{\text{el}}^{\text{CHP}} = E_{\text{el}}^{\text{ref}} + CR \times \Omega \times \hat{E}_{\text{el}}^{\text{CHP}} \quad (\text{S5})$$

$$E_{\text{fuel}} = \frac{E_{\text{th}}^{\text{tot}}}{\eta_{\text{th}}} + \frac{E_{\text{el}}^{\text{tot}}}{\eta_{\text{el}}} \quad (\text{S6})$$

$$\dot{m}_{\text{CO}_2}^{\text{CHP}} = E_{\text{fuel}} \times DEI \quad (\text{S7})$$

$$\dot{m}_{\text{CO}_2}^{\text{CHP}} - \Omega = 0 \quad (\text{S8})$$

Alternatively, an explicit expression for the CO₂ emissions from the CHP plant is given by:

$$\dot{m}_{\text{CO}_2}^{\text{CHP}} = \frac{\left(\frac{E_{\text{th}}^{\text{ref}}}{\eta_{\text{th}}} + \frac{E_{\text{el}}^{\text{ref}}}{\eta_{\text{el}}} \right) \times DEI}{\left[1 - CR \times \left(\frac{\hat{E}_{\text{th}}^{\text{CHP}}}{\eta_{\text{th}}} + \frac{\hat{E}_{\text{el}}^{\text{CHP}}}{\eta_{\text{el}}} \right) \times DEI \right]} \quad (\text{S9})$$

- The residual emissions of the CHP plant, and scope 2 emissions of the fuel source (TIE) can be calculated next:

$$RE^{\text{CHP}} = (1 - CR) \times \Omega \quad (\text{S10})$$

$$TIE = E_{\text{fuel}} \times IEI \quad (\text{S11})$$

- Lastly, the total residual emissions (TRE), total CO₂ avoided (CDA), and CO₂ avoidance rate (CDAR) can be determined:

$$TRE = RE^{\text{ref}} + RE^{\text{CHP}} \quad (\text{S12})$$

$$\dot{m}_{\text{CO}_2}^{\text{tot}} = \sum_i^{\text{sources}} \dot{m}_{\text{CO}_2,i} \quad (\text{S13})$$

$$CDA = \dot{m}_{\text{CO}_2}^{\text{tot}} - TIE - TRE \quad (\text{S14})$$

$$CDAR = \frac{CDA}{\dot{m}_{\text{CO}_2}^{\text{tot}}} \quad (\text{S15})$$

3.2 Emission intensities

- The direct emissions of natural gas ($56.64 \text{ kgCO}_2 \cdot \text{GJ}_{\text{LHV}}^{-1}$) are taken from BEIS (2020).
- The scope 2 emissions of British natural gas ($4.9 \text{ kgCO}_2 \cdot \text{GJ}_{\text{LHV}}^{-1}$) are taken from EcoInvent (Wernet et al., 2016).
- The global average of scope 2 emissions for natural gas ($14.9 \text{ kgCO}_2 \cdot \text{GJ}_{\text{LHV}}^{-1}$) is taken from Balcombe et al. (2015).
- The scope 2 emissions of LNG ($22.0 \text{ kgCO}_2 \cdot \text{GJ}_{\text{LHV}}^{-1}$) are taken from Schuller et al. (2019), who used a GWP_{100} for CH_4 of 30 in their work. Thus, these emissions are likely to be an underestimate compared to the recommended value of 34 (Myrhe et al., 2013).
- The scope 2 emissions of blue H_2 are derived from data in Collodi et al. (2017), and the above emissions of natural gas. Equation S16 is derived from these data assuming negligible impacts from construction of the plant and CCS infrastructure; i.e., only direct emission releases and indirect supply chain emissions of the process. It is based on a CO_2 capture rate of 90% on the reformer flue gas.

$$CI_{\text{H}_2} = 8.22 + 1.44573 \times CI_{\text{NG}} \quad (\text{S16})$$

- The scope 2 emissions of green H_2 ($6.67 \text{ kgCO}_2 \cdot \text{GJ}_{\text{LHV}}^{-1}$) are derived from Cetinkaya et al. (2012). Their estimate of $0.970 \text{ kgCO}_2 \cdot \text{kg}_{\text{H}_2}^{-1}$ was adjusted to exclude the emissions due to H_2 compression and storage, resulting in a value of $0.800 \text{ kgCO}_2 \cdot \text{kg}_{\text{H}_2}^{-1}$.
- Where necessary, HHV to LHV conversions were undertaken using a factor of 1.109 for natural gas, and 1.183 for H_2 .

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