



Refinery integration, scale-up and certification
for aviation and marine biofuels production

D5.4 - Model description FCC and extension to Co-FCC



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Executive summary

Co-feeding of Pyrolysis Oil (PO) together with conventional Vacuum Gas Oil (VGO) in Fluid Catalytic Crackers (FCC) is seen as a promising pathway to effectively process raw bio-derived oils improving their quality, properties, and composition, taking advantage of the already existing infrastructure. In this context, novel modelling approaches and strategies must be investigated to describe and optimize the co-feeding process when dealing with different feedstock composition and operating conditions.

After an introductory presentation of the state of the art of the FCC modelling approaches adopted so far in previous published works, this report describes the objectives and the adopted methodology for the development and validation of a simplified lumped model able to effectively describe the mass and energy balance in combined VGO and PO cracking.

Noteworthy, the target of this report is only the description of the methodology SINTEF plans to adopt for both the development and the validation of the co-feeding FCC model. At the current status of the project, numerical results are not available yet. Indeed, the following two activities must be completed before proceeding with the validation of the modelling approach: (1) the definition of the optimal combination of analytics techniques (e.g., mass spectroscopy, gas chromatography) to characterize the samples chemical composition, and (2) the analytics quantification for all the feed and product samples collected from partners.

Description of the deliverable content and purpose

This report describes the objectives and the adopted methodology for the development and validation of a simplified lumped model able to effectively describe the mass and energy balance in combined VGO and PO cracking.

Deviation from objectives

No deviation is currently observed from the objectives as stated in the GA.

Corrective actions (if relevant)

No specific corrective actions required for the work presented in this report.

Introduction

A Fluid Catalytic Cracking (FCC) model is a relevant and useful tool to predict how feedstock conversion and the yield of the most relevant cuts for commercial applications vary as a function of both the feedstock composition and the adopted operating conditions. Achieving a sufficiently accurate prediction of the FCC product composition is an essential premise for process optimization, maximisation of the most valuable products yield (i.e., gasoline, diesel, kerosene fraction), minimization of waste as well as energy requirements. Ultimately, the FCC model drives the design of an optimized process when handling different feedstocks and operational constraints, targeting as a final aim the minimization of investment and operational costs, as well as the reduction of the carbon footprint of fuel production.

FCC is a key unit operation in several major industrial sectors, including oil refineries, polymer synthesis, as well as recovery and recycling of carbon-rich materials such as plastics. Given the wide interest and application of FCC in the industrial environment, extensive research has already been carried out to develop smart tools for FCC modelling within a process simulator.

The vast majority of the proposed approaches share a common feature: the model must be simple enough to handle the huge complexity of the system within a process flowsheet (e.g., the presence of thousands of different chemical species and the difficult characterization of physicochemical properties), but at the same time it must be sufficiently accurate to predict the most relevant effects of input changes on the product distribution, with minimum deviation.

In this context, the available studies are mainly focused on the characterization of pure Vacuum Gas Oil (VGO) cracking, which to date still represents the common FCC feedstock in refineries. Pure VGO is a relatively simple feedstock, since it mainly contains only carbon and hydrogen, with minor amounts of oxygen, nitrogen, and sulphur. However, very little investigation has been done for more complex feedstocks such as the bio-based oils, which include also significant amounts of oxygen in their elemental composition.

In the REFOLUTION project one of our core aims is to investigate the effect of co-feeding in FCC conventional VGO together with Pyrolysis Oil (PO) and/or Stabilized Pyrolysis Oil (SPO) sourced from biomass pyrolysis. Indeed, the co-feeding technique is seen as a good route to the deployment of advanced biofuels production and to the significant enhancement of pyrolysis oil-derived fuel quality, while preventing the technical issues and challenges that would be encountered when processing pyrolysis oil alone in a dedicated biorefinery [1], [2], [3], [4].

The aim of the work carried out by SINTEF and presented in this report is to start from the existing literature background and develop smart model framework strategies to guarantee an accurate description of FCC units treating a mixture of conventional VGO and PO, predicting also for the effect of different VGO/PO ratios on the product distribution.

1. Methodology for lumped models

Lumping is a well-known modelling strategy attempting to reduce the complexity of a rigorous model while preserving the core physical and chemical relationships that allow a sufficiently accurate characterization of the system [5]. More specifically, lumped models are set up by grouping together several chemical compounds characterized by similar physicochemical properties, for example boiling point or molecular weight, and chemical functionality (e.g., acids, alcohols, aldehydes, etc). All these components form a so-called lumped class. A lumped class is therefore not associable to any exact chemical formula, but it can be characterized by a range of boiling points, molecular weight, and the presence of specific functional groups. To further reduce

the system complexity, a peculiar kind of lumped strategy called Lumped Kinetic Modelling is often adopted in complex reactive environments where an undefined number of elementary reactions take place. In a lumped kinetic model, elementary reactions are grouped into either one or a few apparent reactions, which is/are used to define the overall mass balance of the system. Typical examples of very complex chemical environments where lumped kinetic models find most application are undoubtedly biomass pyrolysis, gasification [6], Fischer-Tropsch synthesis, Hydrothermal Liquefaction [7] and Fluid Catalytic Cracking [8], [9], [10].

1.1. Literature background on lumped models for FCC

Multiple lumped kinetic models have been proposed by several authors to deal with the process design, modelling, and scale-up of FCC. All these FCC models are based on representative lumped chemical classes, which essentially define the different boiling point cuts obtained through FCC product distillation. What differentiates the proposed models is just the number of chemical classes they include, which also defines how detailed the model is. Differentiating the FCC product into a larger number of classes is relevant as long as it allows the quantification and differentiation of fractions that have a specific role and/or application in the downstream treatment. For example, differentiating between LPG (C3-C4 fraction), gasoline, kerosene, and heavy diesel cuts is relevant given that the three have different markets and different selling prices. In this context, a more detailed lumped model can be used to develop different scenarios targeting the maximization of one or another fuel.

Selalame and coworkers provide an overview of the most relevant published FCC lumped models [11]. The most simplified model is a three-lumped model, developed by Weekman and Nace [12], [13], which distinguishes only between VGO, Light Gas and Coke, and Gasoline. Lee et al. [14] modified the model by Weekman and Nace introducing a differentiation between coke and light gases, which have been split into two separate lumped classes. Multiple examples of models including a larger number of classes can be mentioned:

- Ancheyta-juarez and coworkers [15] as well as Hollander and coworkers [16] developed a 5-lump model with 7 chemical reactions, where Low-Fuel oil (LFO) and Heavy-Fuel Oil (HFO) are distinguished.
- Ebrahimi et al. [17] proposed a 9-lump model which differentiates between normal-paraffins, iso-paraffins, olefins, aromatics, coke, C4 olefines, C40 hydrocarbons, C₂₋₃ olefines, and H₂ + C₁₋₃ lumps.
- Jacob et al. [18] formulated a 10-lump model (see Figure 1), which distinguishes between light and heavy fractions of paraffines, naphthalenes, aromatic substitutes and aromatic rings.
- Du et al. [19] proposed another 10-lump model which splits the products into the following: heavy oil (HO), diesel oil (DO), gasoline olefines (GO), gasoline aromatics (GA), gasoline saturates (GS), butane + propane (C3-4), butylene (C4=), propylene (C3=), dry gas (DG), and coke (CK). A sketch of the model is depicted in Figure 2. Noteworthy, this is the only model that strengthens the importance of differentiating saturated and unsaturated C3 and C4 hydrocarbons based on their relevant specific markets.

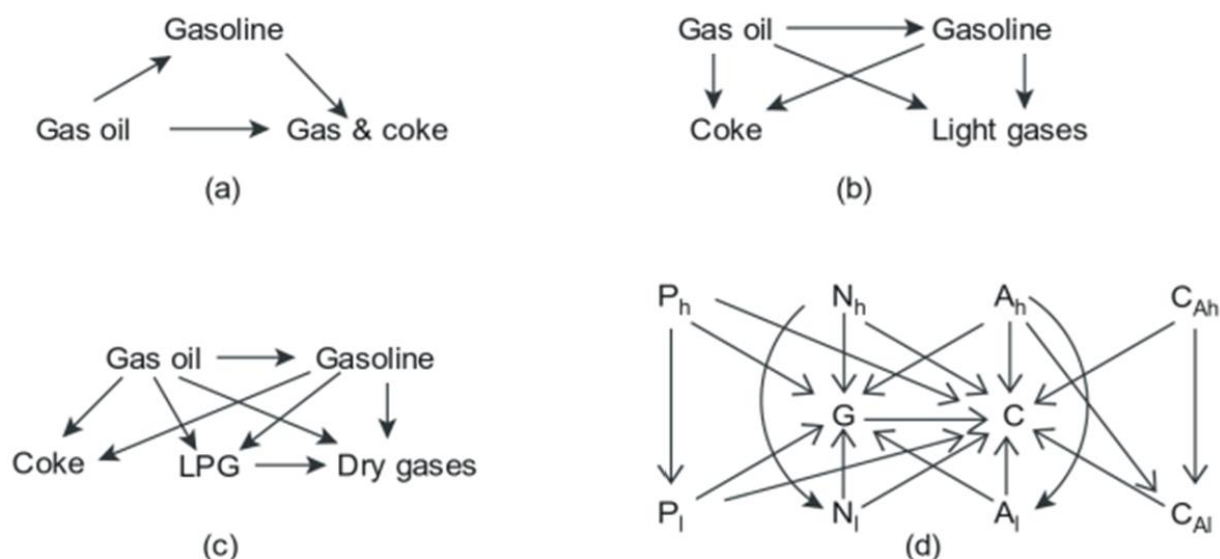


Figure 1. Examples of lumped models for FCC modelling published in previous works: (a) 3-lump model by Weekman and Nace, (b) 4-lump model by Lee et al., (c) 5-lump model by Ancheyta-Juarez et al., and (d) 10-lump model by Jacob et al. Retrieved from Selalame et al. [11]

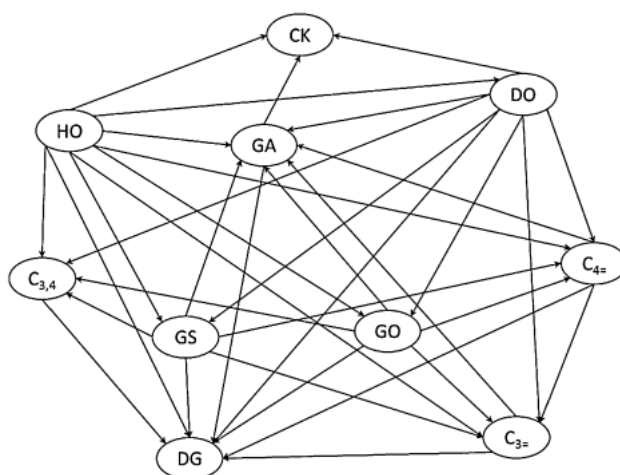


Figure 2. 10-lump FCC model developed by Du et al., 2015.

The higher the number of lumped species considered, the larger the number of experimental data required for proper tuning of the model without overfitting issues.

In each model, several Arrhenius-type kinetic expressions are proposed, each describing the conversion of one lumped class into another one as a function of the temperature as well as of the reactant concentration in the system. It is noteworthy to mention that all the abovementioned lumped kinetic models including at least four lumped classes are able to describe also the formation and decomposition of intermediates as a function of the residence time. Indeed, it is known from FCC operational experience that, if a sufficiently long residence time is provided inside the FCC chamber, part of the gasoline, kerosene, and diesel can further decompose generating light gases and coke.

To account for this, lumped kinetic models include not only dedicated chemical reactions to define fuels (gasoline, diesel, and kerosene) formation from VGO, but also further reactions specifically tuned to describe

the expected decomposition of part of the formed fuels into either light gases or coke formation.

1.2. From lumped kinetics to lumped conversion model

Despite their great potentiality and their ability to describe intermediates formation, lumped kinetic models require a relatively complex Design of Experiments and cannot be tuned and validated in the absence of data describing both temperature and composition profiles. In other words, it is not sufficient to measure the composition of the feedstock and of the product leaving the FCC following an input-output approach. It is instead mandatory to collect multiple temperature and composition measurements at different points along the FCC packing height.

Considering that this kind of data cannot be provided by the partners responsible of experimental campaign on both smaller and larger scale in the project due to the intrinsic limitations of the experimental apparatus, SINTEF decided to shift from a lumped kinetic model to a lumped conversion model. A sketch of the structure of a generic lumped conversion and of that of a lumped kinetic model is drawn in Figure 3 to better visualize what differentiates the two approaches and why is the conversion-based model more suitable to handle the data collected within REFOLUTION.

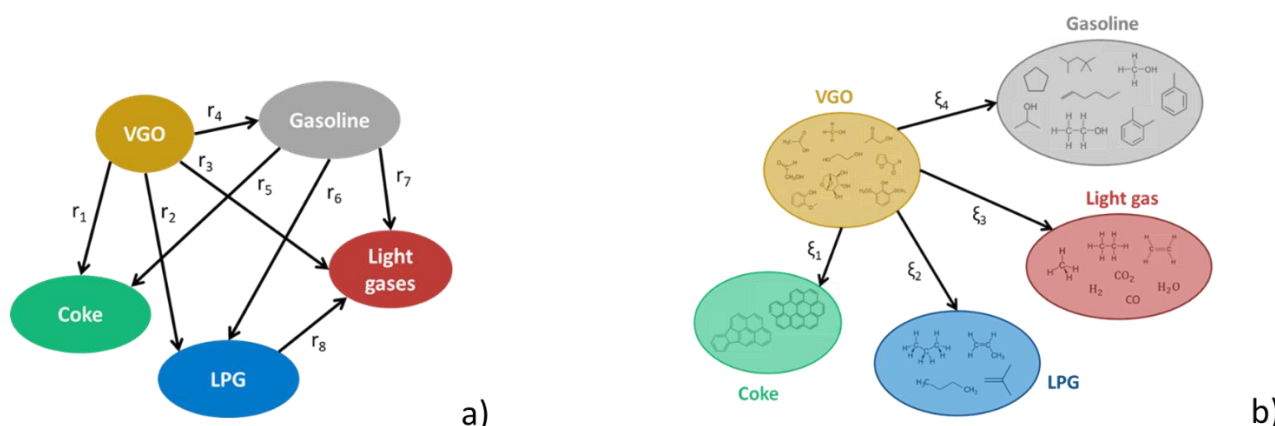


Figure 3. Schematic diagram of (a) lumped kinetic model, and (b) lumped conversion model for FCC.

The conversion-based model handles exactly the same number and types of the corresponding kinetics-based model. However, the conversion model is simply an input-output model, with no description of the intermediates. Indeed, in the conversion model the only considered reactions are the ones describing the conversion of VGO into each of the identified lumped classes of the FCC product. Conversely, the kinetic-based model includes a much larger number of reactions for a given set of lumped classes, since VGO is not the only reactant. For example, gasoline and other classes considered as intermediates such as LPG can be further decomposed into light gases and coke. As a consequence, the conversion model is the only approach compatible with the absence of temperature and composition profiles.

In addition, the conversion-based model is much more flexible. Indeed, the conversion for each lumped reaction can be defined as a function of those operating conditions whose variation is known to significantly affect the conversion as well as the yield of the most high-value products. A response curve for the conversion in each reaction can be tuned to in-house data collected by varying each time only one of the operating conditions whose effect is to be tested and keeping all the others fixed.

Moreover, being the conversion model simpler and characterized by a reduced number of degrees of freedom,

strategies can be adopted to predict also a rough estimate of the chemical composition of each lump class accounting for representative real molecules. Further details on this are available in section 2.

Last but not least, the tuning of conversion-based model to experimental data can be performed using simple regression algorithms and does not require non-linear regression of ODE systems. On the other hand, its main limitation is that it is fully data-driven, which makes it impossible to extrapolate it under the investigated range of feedstocks composition and operating conditions.

A more extensive summary of how a conversion-based model differentiates from a kinetic-based one is reported in Table 1.

Table 1. Comparative features of a kinetic-based and a conversion-based FCC model.

Property	Kinetic model	Conversion model
Molecules	Not defined expect for light gas “class”	Most relevant and exemplifying are characterised
Measurements	Multiple along the riser height	Only at the input and output of the FCC process
Outcomes	Profile for temperature and cuts	Only input-output model (product distribution)
Number of variables	Arrhenius parameters	One conversion index per reaction
Validity	Could be general (depending on the feedstock impact)	Not extendible outside the domain of investigation
Numerical approach	Nonlinear regression of an ODE system	Multivariable optimization (probably linear)

2. Modelling approach

This section describes the approach and the assumptions adopted to develop an FCC model suitable for the targets of REFOLUTION. The core of the model is based on a conversion-based approach and on a lumping strategy, where the most relevant lump classes are identified in compliance with the literature and according to the criteria and targets stated in section 1. However, the reliability of a model must be checked through validation to real data. This validation cannot be done based on lump classes directly, since, whatever technique is adopted to carry out analytics on samples collected during plant operation, the analytics results are always provided in terms of real molecules. Therefore, smart criteria must be adopted to be able to predict a rough estimate of the composition of each lump class through the identification of the most representative molecules.

Based on these considerations, we developed a model whose structure can be divided into three steps:

1. De-lumping phase for the reactants. Representative chemical compounds are identified to characterize both VGO and PO. This preliminary selection of relevant compounds is performed based on the outcomes of the analytics carried out on some default VGO and PO feed samples as well as on the published literature. Then, the composition of the VGO and PO, namely the relative content of each of the identified representative molecules, is calculated using an optimization algorithm. The objective function is the minimization of the deviation between model prediction and experimental

data on the atomic balances for carbon, hydrogen, and oxygen atoms.

2. Lumping phase. The number and type of lump class is selected in compliance with the level of detail allowed by the available experimental setup. Then, a dedicated conversion expression is defined for VGO transforming into each of the identified lump. This conversion is defined as a mathematical expression that accounts for the dependency on key operating conditions (see section 2.1.2).
3. De-lumping phase for the products. Representative chemical species are identified for each lump class, based on previous literature and preliminary results from analytics. The composition of each lump class is then tuned by minimizing the deviation on atomic balances, following the same procedure described for the reactants in point 1).

2.1. Model framework for pure VGO cracking

2.1.1. Identified lump classes and reactions

In our work, we decided to deal with a 6-lump model approach for the pure VGO cracking model. The considered lump classes, which have been selected in accordance with the level of detail of the experimental data on FCC product composition shared by CEPISA, are:

- VGO (reactant)
- Light gases (LG)
- LPG (C_{3,4})
- Gasoline (GA)
- Diesel (DI)
- Coke (CK)

VGO is the only lump class describing the feed, while all the others define specific product cuts of the FCC. Therefore, the lumped reaction scheme can be formulated as in Table 2:

Table 2. List of reactions embodied in the lump class conversion-based model.

Reaction ID	Expression
R1	$VGO \rightarrow LG$
R2	$VGO \rightarrow LPG$
R3	$VGO \rightarrow GA$
R4	$VGO \rightarrow D$
R5	$VGO \rightarrow CK$

2.1.2. Design of experiments for model tuning

A crucial step towards the FCC model development is setting up an optimal design of experiments (DoE) that allows to match the theoretical needs of a lumped conversion model with the practical constraints and potentiality of the experimental apparatus owned by the project partners. We emphasize that the DoE has been discussed between SINTEF and all the project partners responsible of running the experimental campaigns during dedicated workshops organized as side events of the M18 and M24 project meeting.

The identified operating conditions for which a dedicated response curve will be developed in the conversion model are:

- Temperature of the catalyst (T)
- Positioning of the PO feed along the FCC bed (PosF)
- the Catalyst to Oil ratio (CTO)

For each reaction (i), the conversion (X_i) minimizing the deviation between the model and exp. data is obtained as a function of all the mentioned operating conditions (see expression (1), where NR stands for the total number of reactions embodied in the lumped model).

	$X_i = f(T, \text{PosF CTO})$ with $i = 1, 2, \dots, \text{NR}$	(1)
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2.1.3. The de-lumping phase: compounds identification

2.1.3.1. Feed

The identification of the representative compounds for pure VGO has been performed based on considerations about the minimum, maximum, and average carbon chain lengths of the molecules as well as on the type of predominately present molecules (e.g., aromatics, naphthalenes, and saturated hydrocarbons). These pieces of information have been retrieved from the literature [20], [21]. For confirmation, SINTEF has performed analytics on a couple of reference VGO samples using GC-FID (Gas Chromatography- Fluid Ionization Detector) technique. Results show that over 95% of the molecules have a carbon chain length between C_{20} and C_{30} .

The selected components for VGO characterization are gathered in Table 3.

Table 3. List of the representative molecules selected to characterize the composition of pure VGO.

Component name	Component type	Component formula
Tetracosane	C_{24} alkane	$C_{24}H_{50}$
triacontane	C_{30} alkane	$C_{30}H_{62}$
Corannulene	C_{20} polycyclic aromatic	$C_{20}H_{10}$
Indeno(1,2,3-cd)pyrene	C_{22} polycyclic aromatic	$C_{22}H_{12}$
Coronene	C_{24} polycyclic aromatic	$C_{24}H_{12}$
Naphtho[8,1,2-abc]coronene	C_{30} polycyclic aromatic	$C_{30}H_{14}$

2.1.3.2. Product

Light gas contains all the molecules that are known to form in a FCC and whose boiling point is lower than ambient temperature: these include C_1 , C_2 hydrocarbons, and hydrogen. For the sake of simplicity, coke can be assumed as pure carbon. The identification of key molecules to describe the composition of LPG, gasoline, and diesel fractions has been performed based on the following considerations:

- LPG consists mainly of propane (C_3H_8) and butane (C_4H_{10}) but may in addition contain some

percentage volumes of the unsaturated components propene and butene [22].

- The hydrocarbons of gasoline contain typically from 4 up to 12 carbon atoms, with a boiling range between 30 °C and 210 °C [23].
- Diesel contains hydrocarbons with approximately 12 to 20 carbon atoms and the boiling range is between 170 and 360 °C [23].
- The typical composition of gasoline hydrocarbons (% volume) is as follows: 4-8% alkanes; 2-5% alkenes; 25-40% isoalkanes; 3-7% cycloalkanes; 1-4% cycloalkenes; and 20-50% total aromatics (0.5-2.5% benzene). Composition data are retrieved from IARC [24].
- Diesel consists of approximately 75% aliphatic hydrocarbons ($C_{10}H_{20}$ – $C_{15}H_{28}$) and about 25% aromatic hydrocarbons (e.g. benzene, styrene). The typical atomic mass concentrations are about 86% C, 14% H, and a minor fraction of sulphur, which depends on the crude oil source and cleaning quality [22].

Table 5 gathers a comprehensive list of all the representative molecules that have been selected for the characterization of the composition of each lump class.

Table 4. List of the representative molecules selected for the characterization of the composition of each lump class.

Lump class	Component name	Component type	Component formula	Boiling point (°C)
LG	Hydrogen		H ₂	-252.5
LG	Methane		CH ₄	-161.5
LG	Ethane	C ₂ alkane	C ₂ H ₆	-89
LG	Ethylene	C ₂ alkene	C ₂ H ₄	-103.7
LPG	Propane	C ₃ alkane	C ₃ H ₈	-42
LPG	Butane	C ₄ alkane	C ₄ H ₁₀	-1
LPG	Propylene	C ₃ alkene	C ₃ H ₆	-47.6
LPG	Butylene	C ₄ alkene	C ₄ H ₈	-6.3
GA	Cyclopentane	C ₅ - cyclic	C ₅ H ₁₀	49.2
GA	Isooctane	C ₈ - isoalkanes	C ₈ H ₁₈	99
GA	1-hexene	C ₆ - hexene	C ₆ H ₁₂	63
GA	1-octene	C ₈ - octene	C ₈ H ₁₆	121
GA	Toluene	C ₇ aromatics	C ₇ H ₈	110.6
GA	Xylene	C ₈ - aromatics	C ₈ H ₁₀	139.3
DI	Naphtalene	C ₁₀ -aromatic	C ₁₀ H ₈	218
DI	Pentadecene	C ₁₅ alkene	C ₁₅ H ₃₀	269
DI	Eicosane	C ₂₀ alkane	C ₂₀ H ₄₂	343

2.2. Extension to co-FCC

The model concept developed for VGO and described in paragraph 2.1 is general and can be easily applied also for a different feedstock, such as PO, with only minor modifications.

For the lumping phase, no modifications are required. For the de-lumping phase, the list of representative components for both the feedstock and the FCC product requires instead an integration. Indeed, the main difference when dealing with PO as a feedstock is the presence of oxygen in considerable amounts in the feedstock. Noteworthy, the presence of oxygen in the feedstock also results in the formation of oxygenated

products from the FCC, such as CO, CO₂, light ketones, alcohols, and phenols.

As a matter of fact, molecules containing only C and H as atoms cannot provide a full picture of the feedstock as well as the products. To handle this increased level of complexity in the model and correctly address also the oxygen balance, some representative oxygenated compounds whose presence is expected to be relevant in raw PO as well as those forming from PO cracking have been identified.

2.2.1. Identified lump classes

All the lump classes selected for the lumped VGO cracking model (see section 2.1.1) identify a specific cut of the FCC product. This occurs because, when dealing with FCC simplified models, the main interest is to address how much gasoline-like or kerosene-like components are obtained, rather than getting a detailed picture of the chemical composition.

According to this approach, the boiling point (or molecular weight) is the only criterion to define the correct lumped class a specific chemical compound belongs to. This means that there is no differentiation according to the elemental composition (i.e., C, O, and H content) or the functional groups. In this context, the six lump classes identified for the pure VGO cracking model still apply also to the co-feeding of PO. However, there is need to add water as additional lump class. Indeed, water formation is expected to be relevant in presence of oxygen in the feedstock, and it cannot be included in any of the other lump due to its boiling point and physicochemical properties. The addition of water in the lumped model results also in the introduction of a further reaction in the lumped reaction scheme, called R6.

	$VGO \rightarrow H_2O$	R6
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2.2.2. Design of experiments for model tuning

The same procedure described in section 2.1.2 is repeated varying the PO content in the feed. For the sake of consistency with the approach followed by CEPSSA during the experimental campaigns, the following three feedstock compositions are planned to be tested for the sake of model development and validation:

- pure VGO
- 4% PO – 96% VGO
- 8% PO – 92% VGO

2.2.3. The de-lumping phase: compounds identification

2.2.3.1. Feed

The characteristic molecules defining a rough estimate of the chemical composition of PO have been selected based on experimental data on PO composition and other lumped models for fast pyrolysis published in previous works [6], [25], [26]. It is noteworthy to mention that the component list embodies oxygenates, whose relevance is stated in 2.2. A list of the selected components is reported in Table 5.

Table 5. List of the representative molecules selected to characterize the composition of PO feedstock.

Component name	Component type	Component formula	Boiling point (°C)
Acetic acid	Acids	C ₂ H ₄ O ₂	117.9
Methanol	Alcohols	CH ₄ O	64.7
Ethylene glycol	Alcohols	C ₂ H ₆ O ₂	197.3
Hydroxyacetaldehyde	Carbonyls	C ₂ H ₄ O ₂	131.3
Hydroxypropanone	Carbonyls	C ₃ H ₆ O ₂	145.0
Levogluconan	Sugar-type	C ₆ H ₁₀ O ₅	384.0
Furfural	Furan	C ₅ H ₄ O ₂	161.7
Guaiacol	Lignin LMM	C ₇ H ₈ O ₂	205.0
Syringol	Lignin LMM	C ₈ H ₁₀ O ₃	261.0
High molecular weight Lignin	Lignin HMW + extractives	C ₂₄ H ₂₈ O ₄	800.0

2.2.3.2. Product

For the characterization of the FCC product in the presence of PO in the feed, all the chemicals used in the model for pure VGO and listed in Table 4 are still embodied in the model. They still provide a good overview of the product distribution in terms of carbon and hydrogen balance. However, oxygenates product must also be introduced in the compounds list. These have been selected as the most likely forming oxygen-containing products based on the observations collected during co-feeding sample analytics in SINTEF. The identified components have been assigned to a specific lump class simply based on their boiling point. A list of all the oxygenated species introduced to extend the FCC model to the co-feeding of PO is available in Table 6.

Table 6. List of the oxygenated species embodied in the lumped model for combined VGO and PO cracking.

Lump class	Component name	Component type	Component formula	Boiling point (°C)
Water	Water		H ₂ O	100.0
LG	Carbon monoxide		CO	-191.5
LG	Carbon dioxide		CO ₂	-78.46
GA	Methanol	Alcohol	CH ₄ O	64.7
GA	Ethanol	Alcohol	C ₂ H ₆ O	78.37
GA	Iso-propanol	Alcohol	C ₃ H ₈ O	82.3
GA	Acetone	Ketone	C ₃ H ₆ O	56.0
GA	Butanone	Ketone	C ₄ H ₈ O	79.6
DI	Phenol	Phenolic	C ₆ H ₆ O	181.7
DI	Cresol	Phenolic	C ₇ H ₇ O	202

3. Future developments

The model framework described in this report will be validated to real data in the second part of the project (M25 – M42). More specifically, the validation will be done considering both experimental data collected from CEPISA and BTG and based on the results of sample analytics to be performed within Task 5.2 in SINTEF. To guarantee reliable results, directly correlated feed and product samples collected during the same runs will be analysed.

After the accomplishment of model validation, the model will be implemented in COCO-COFE (Cape Open-Cape Open- Cape Open Flowsheet Environment), a license-free process simulator. The mass and energy balance obtained from the process simulation will be used to achieve the following targets in Task 5.3:

- Optimal FCC operation design to maximise VGO and VGO/PO conversion and maximise the yield of gasoline and/or kerosene fraction. The optimization will concern both feedstock composition and operating conditions of the FCC unit;
- Techno-economic assessment of the process.

Conclusions

A model framework has been developed for the sake of process design and optimization of an FCC unit within a license-free process simulation. The proposed approach is general and can be easily extended to different feedstocks. A dedicated strategy is proposed to align the model to the peculiarities of an FCC operated with the co-feeding of VGO and PO. In particular, the presence of oxygen in the PO feedstock is identified as the major difference requiring modifications with respect to a cracking process run by processing only conventional VGO.

At the current status, only the model structure and a specific plan for its validation over plant data are available. A full validation of the proposed approach is required before using the model for the sake of process design and optimization. This step will be achieved in the second part of the project, based on the input that will be progressively collected from the sample analytics and from the pilot plants operation.

References

- [1] A. A. Lappas, S. Bezergianni, and I. A. Vasalos, 'Production of biofuels via co-processing in conventional refining processes', *Catal. Today*, vol. 145, no. 1–2, pp. 55–62, Jul. 2009, doi: 10.1016/j.cattod.2008.07.001.
- [2] X. Han, H. Wang, Y. Zeng, and J. Liu, 'Advancing the application of bio-oils by co-processing with petroleum intermediates: A review', *Energy Convers. Manag. X*, vol. 10, p. 100069, Jun. 2021, doi: 10.1016/j.ecmx.2020.100069.
- [3] C. Lindfors, D. C. Elliott, W. Prins, A. Oasmaa, and J. Lehtonen, 'Co-processing of Biocrudes in Oil Refineries', *Energy Fuels*, vol. 37, no. 2, pp. 799–804, Jan. 2023, doi: 10.1021/acs.energyfuels.2c04238.
- [4] Asmaa. A. M. Ali, Mustafa. A. Mustafa, and K. E. Yassin, 'A techno-economic evaluation of bio-oil co-processing within a petroleum refinery', *Biofuels*, vol. 12, no. 6, pp. 645–653, Jul. 2021, doi: 10.1080/17597269.2018.1519758.
- [5] S.-M. Lorbach, A. E. Lechleitner, F. Zapf, and M. Lehner, 'Usefulness of Lumped Kinetic Modeling', *Chem Bio Eng.*, vol. 1, no. 7, pp. 623–632, Aug. 2024, doi: 10.1021/cbe.4c00032.
- [6] E. Ranzi, M. Corbetta, F. Manenti, and S. Pierucci, 'Kinetic modeling of the thermal degradation and combustion of biomass', *Chem. Eng. Sci.*, vol. 110, pp. 2–12, May 2014, doi: 10.1016/j.ces.2013.08.014.

- [7] D. Forchheim, U. Hornung, A. Kruse, and T. Sutter, 'Kinetic Modelling of Hydrothermal Lignin Depolymerisation', *Waste Biomass Valorization*, vol. 5, no. 6, pp. 985–994, Dec. 2014, doi: 10.1007/s12649-014-9307-6.
- [8] W. Zhao *et al.*, 'Eight-lumped kinetic model for Fischer-Tropsch wax catalytic cracking and riser reactor simulation', *Fuel*, vol. 308, p. 122028, Jan. 2022, doi: 10.1016/j.fuel.2021.122028.
- [9] E. Ranzi, M. Dente, A. Goldaniga, G. Bozzano, and T. Faravelli, 'Lumping procedures in detailed kinetic modeling of gasification, pyrolysis, partial oxidation and combustion of hydrocarbon mixtures', *Prog. Energy Combust. Sci.*, vol. 27, no. 1, pp. 99–139, Jan. 2001, doi: 10.1016/S0360-1285(00)00013-7.
- [10] L. P. de Oliveira, D. Hudebine, D. Guillaume, and J. J. Verstraete, 'A Review of Kinetic Modeling Methodologies for Complex Processes', *Oil Gas Sci. Technol. – Rev. D'IFP Energ. Nouv.*, vol. 71, no. 3, Art. no. 3, May 2016, doi: 10.2516/ogst/2016011.
- [11] T. W. Selalame, R. Patel, I. M. Mujtaba, and Y. M. John, 'A Review of Modelling of the FCC Unit–Part I: The Riser', *Energies*, vol. 15, no. 1, p. 308, Jan. 2022, doi: 10.3390/en15010308.
- [12] V. W. Weekman, 'Model of Catalytic Cracking Conversion in Fixed, Moving, and Fluid-Bed Reactors', *Ind. Eng. Chem. Process Des. Dev.*, vol. 7, no. 1, pp. 90–95, Jan. 1968, doi: 10.1021/i260025a018.
- [13] V. W. Weekman Jr. and D. M. Nace, 'Kinetics of catalytic cracking selectivity in fixed, moving, and fluid bed reactors', *AIChE J.*, vol. 16, no. 3, pp. 397–404, 1970, doi: 10.1002/aic.690160316.
- [14] L.-S. Lee, Y.-W. Chen, T.-N. Huang, and W.-Y. Pan, 'Four-lump kinetic model for fluid catalytic cracking process', *Can. J. Chem. Eng.*, vol. 67, no. 4, pp. 615–619, 1989, doi: 10.1002/cjce.5450670414.
- [15] J. Ancheyta-Juárez, F. López-Isunza, E. Aguilar-Rodríguez, and J. C. Moreno-Mayorga, 'A Strategy for Kinetic Parameter Estimation in the Fluid Catalytic Cracking Process', *Ind. Eng. Chem. Res.*, vol. 36, no. 12, pp. 5170–5174, Dec. 1997, doi: 10.1021/ie970271r.
- [16] M. A. den Hollander, M. Makkee, and J. A. Moulijn, 'Coke formation in fluid catalytic cracking studied with the microriser', *Catal. Today*, vol. 46, no. 1, pp. 27–35, Nov. 1998, doi: 10.1016/S0920-5861(98)00348-4.
- [17] A. Afshar Ebrahimi, H. Mousavi, H. Bayesteh, and J. Towfighi, 'Nine-lumped kinetic model for VGO catalytic cracking; using catalyst deactivation', *Fuel*, vol. 231, pp. 118–125, Nov. 2018, doi: 10.1016/j.fuel.2018.04.126.
- [18] S. M. Jacob, B. Gross, S. E. Voltz, and V. W. Weekman Jr., 'A lumping and reaction scheme for catalytic cracking', *AIChE J.*, vol. 22, no. 4, pp. 701–713, 1976, doi: 10.1002/aic.690220412.
- [19] Y. Du, Q. Yang, C. Zhang, and C. Yang, 'Ten-lump kinetic model for the two-stage riser catalytic cracking for maximizing propylene yield (TMP) process', *Appl. Petrochem. Res.*, vol. 5, no. 4, pp. 297–303, Dec. 2015, doi: 10.1007/s13203-015-0114-1.
- [20] M. Al-Saleh, 'Hydrogen spillover effects on Pt–Rh modified Co–clay catalysts for heavy oil upgrading', *Appl. Catal. Gen.*, vol. 253, no. 2, pp. 453–459, Oct. 2003, doi: 10.1016/j.apcata.2003.06.001.
- [21] N. Wang, C. Peng, Z. Cheng, and Z. Zhou, 'Molecular reconstruction of vacuum gas oils using a general molecule library through entropy maximization', *Chin. J. Chem. Eng.*, vol. 48, pp. 21–29, Aug. 2022, doi: 10.1016/j.cjche.2021.06.007.
- [22] M. Huth and A. Heilos, '14 - Fuel flexibility in gas turbine systems: impact on burner design and performance', in *Modern Gas Turbine Systems*, P. Jansohn, Ed., in Woodhead Publishing Series in Energy, Woodhead Publishing, 2013, pp. 635–684. doi: 10.1533/9780857096067.3.635.
- [23] 'AMF'. Accessed: Dec. 02, 2024. [Online]. Available: https://www.iea-amf.org/content/fuel_information/diesel_gasoline
- [24] A. Y. E. Naggar *et al.*, 'Hydrocarbon compositions and physicochemical characteristics for the determination of gasoline quality: An implication from gas chromatographic fingerprints', *Energy Sources Part Recovery Util. Environ. Eff.*, vol. 39, no. 15, pp. 1694–1699, Aug. 2017, doi: 10.1080/15567036.2017.1370515.
- [25] A. Oasmaa, J. Lehto, Y. Solantausta, and S. Kallio, 'Historical Review on VTT Fast Pyrolysis Bio-oil Production and Upgrading', *Energy Fuels*, vol. 35, no. 7, pp. 5683–5695, Apr. 2021, doi: 10.1021/acs.energyfuels.1c00177.
- [26] K. Onarheim, Y. Solantausta, and J. Lehto, 'Process Simulation Development of Fast Pyrolysis of Wood Using Aspen Plus', *Energy Fuels*, vol. 29, no. 1, pp. 205–217, Jan. 2015, doi: 10.1021/ef502023y.

