

A chemical kinetics approach for heavy fuel oils gasification modelling

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Abstract

Refinery oil residue commonly considered the bottom of the barrel, can no longer be a waste. The increasing energy demand and the constant depletion of light oil supply make it crucial to find a suitable way to convert residual oils into valuable fuels. The gasification process represents a possible solution to this problem. Gasification is a thermo-process conducted in poor oxygen conditions, intending to obtain a hydrogen and carbon monoxide mixture, commonly named syngas. Gasification is widely implemented on an industrial scale to treat complex combinations such as biomasses, plastic waste, and coal. Most of the studies in the literature approach gasification modelling by studying the chemical equilibrium or with Computational fluid dynamics (CFD). However, the chemical equilibrium approach is well-performing in predicting the major gasification products, like hydrogen, carbon monoxide, carbon dioxide, and water. Thus, missing some crucial information like side-products formation or the evolution of conditions along the reactor, like temperature and species profile. The CFD approach overtakes the problems of the equilibrium approach, thus requiring a high level of complexity and being computationally expensive. The approach here proposed to model heavy oil gasification is based on the definition of a suitable kinetics model to target the evolution of all the essential variables along the reactor, thus with very low computational cost. The gasification process results from three different steps with different characteristic times. The first step is feed pyrolysis; liquid or solid feeds are exposed to very high temperatures. This triggers the thermal-decomposition reactions resulting in the volatilization of the feed in smaller gas molecules and the formation of a solid residue (CHAR). The second step is the partial combustion of gas compounds in homogeneous gas phase reactions. Finally, the last and slowest step is gasifying the solid products generated during the pyrolysis. The modelling approach is based on defining different reactive pathways for the three steps. The major challenge in modelling the first step is defining a proper framework for the feed characterization. A surrogate mixture is used to mimic feed chemical and physical properties. The surrogate is defined according to practical information on the feed; specifically, the SARA (Saturates, Aromatics, Resins, Asphaltenes) analysis and the elemental characterization are used to define the appropriate surrogate starting from a pool of nineteen key molecules. The pyrolysis of each surrogate molecule is described by a first-order irreversible reaction leading to the formation of gas and solid products (CHAR). The partial combustion is then described by coupling a gas phase mechanism. Depending on the required details, the gas phase mechanism can be either detailed or reduced. The gas phase mechanism accounts for the combustion of gas species released during the previous step. The last step describes the gasification of the CHAR generated in the first step, modelled with a series of global reactions defined empirically. The kinetics approach described above allows estimating major gasification products and eventual side products according to the level of details desired. It permits an assessment of much more information that cannot be extrapolated using a chemical-equilibrium approach like the reactor thermal profile and species evolution, and computational cost is much lower than CFD simulations.

Keywords:

surrogate, HFOs, pyrolysis, chemical kinetics modeling, Gasification

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1. Introduction

The increasing energy demand and the constant depletion of light oil supply make it crucial to find a suitable way to convert residual oils into valuable fuels. Gasification is a possible way to convert residual and heavy oils into valuable products, specifically a mixture of hydrogen, carbon monoxide, water, and minor other products, commonly known as syngas. Oils currently used for gasification are heavy or extra-heavy crude oils, atmospheric and vacuum residues, and heavy fuel oils (HFOs). The latter is commonly defined as the blend of vacuum residue with lighter petroleum fractions to improve fuel properties. The gasification process is based on the partial combustion of the fuel in oxidant defect conditions to favour the formation of syngas instead of complete combustion products. The produced syngas can be employed for many applications, like as raw material for chemicals or liquid fuels (Fisher-Tropsch process) synthesis, for direct hydrogen production, or may be combined with a power plant system to make integrated gasification combined cycle[1]. The gasification process is articulated in three sequential steps: Feed pyrolysis; liquid or solid feeds are exposed to very high temperatures. This triggers the thermal cracking reactions resulting in the volatilization of the feed in smaller gas molecules and forming a solid residue (CHAR). The second step is the partial combustion of gas compounds in homogeneous gas phase reactions. The last and slowest step consists of heterogeneous gasification of the solid products generated during the pyrolysis. Nowadays, gasification is widely implemented on an industrial scale to treat complex mixtures such as biomasses, plastic waste, and coal. Very few works focused on applying heavy and residual oils for gasification, both from the experimental and modelling points of view. Two approaches have been mainly adopted in the literature to model a gasifier. The first is based on the chemical equilibrium to determine the final syngas composition neglecting what happens in the reactor. The second is based on Computational Fluid Dynamics (CFD) to account for all the relevant phenomena in the reactor. The chemical equilibrium approach is well-performing in predicting the major gasification products, like hydrogen, carbon monoxide, carbon dioxide, and water. Thus, missing some crucial information like formation side-products or the evolution of conditions along the reactor, like temperature and species profile. The CFD approach overtakes the problems of the equilibrium approach, thus requiring a high level of complexity and being computationally expensive. Choi et al. [2] studied the characteristics of vacuum residue gasification in an entrained flow reactor able to process 1 t/d of fuel. Choi also reported a theoretical study to model the gasifier using the thermodynamics equilibrium approach. More recently, Vaezi et al. [1] proposed a model for HFOs gasification using a thermodynamic approach similar to the one reported by Choi. Conversely, works like Bader et al. [3] and Kumar et al. [4] reported detailed CFD model where all the three process steps are properly accounted for. This way, it is possible to track all the important variables in the reactor, like species and temperature evolution, at the cost of high computational requirements. The approach proposed in this work to model heavy oil gasification is based on the definition of a suitable kinetics model to target the evolution of all the important variables along the reactor, thus with very low computational cost. The modelling approach is based on the definition of different reactive pathways for the three steps of gasification. The major challenge in modelling the first step is defining a proper framework for the feed characterization. A surrogate mixture is used to mimic feed chemical and physical properties. The surrogate is defined according to experimental information on the feed; specifically, the SARA (Saturates, Aromatics, Resins, Asphaltenes) analysis and the elemental characterization are used to define the appropriate surrogate starting from a pool of nineteen key molecules. The pyrolysis of each surrogate molecule is described by a first-order irreversible reaction leading to the formation of gas and solid products (CHAR). The partial combustion is then described by coupling a gas phase mechanism. The gas phase mechanism can be either detailed or reduced, depending on the level of detail required. The gas phase mechanism accounts for the combustion of gas species released during the previous step. The last step describes the gasification of the CHAR generated in the first step, modelled with a series of global reactions defined empirically. Further details about modelling all three steps are reported in the following sections. The model was implemented in ANSYS CHEMKIN R2021 and validated against experimental data reported in the literature.

2. Kinetic Model

2.1. Pyrolysis

The first and most challenging requirement to start modelling the pyrolysis is the definition of a proper feed characterization method. A standard experimental procedure for HFOs characterization is the SARA analysis. SARA analysis separates four fractions: Saturates, Aromatics, Resins, and Asphaltenes from the oil. The fractions are

defined by differences in solubility and polarity among them. The characterization framework proposed in this work is based on the design of a certain number of pseudo components used to generate surrogate mixtures to mimic each SARA fraction. The oil is then reconstructed as the linear combination of the SARA surrogates, ending in a nineteen molecules surrogate. The input data required to initialize the model by generating the surrogate are SARA analysis of the oil sample, the elemental composition of each SARA fraction, and an average estimation of the molecular weight for Saturates and Aromatics. The additional data on the molecular weight for Saturates and Aromatics is required because they are the fractions with the lightest molecules. Thus, other than thermal cracking, evaporation must also be considered for Saturates and Aromatics. The evaporation is accounted for with the average molecular weight data. The pseudo-components used to generate the surrogate mixture derive from comprehensive literature research aimed to create a reasonably comprehensive database to define an operative range, including the widest variety of oil samples. The formulation of the pseudo-components adopted in this work proceeded by accounting for three objectives:

- The surrogate molecules have to conform to the atomic ratios identified using a graphic approach to be suitable for the description of all the experimental data.
- The surrogate molecules are required to have a realistic molecular weight to describe oil's physical properties.
- The surrogate molecules need to have a realistic molecular structure to develop a reliable kinetics model for pyrolysis.

The model for asphaltenes, from surrogate formulation to kinetics mechanism, is here reported as an example. Details for all the other SARA fractions can be found elsewhere [5].

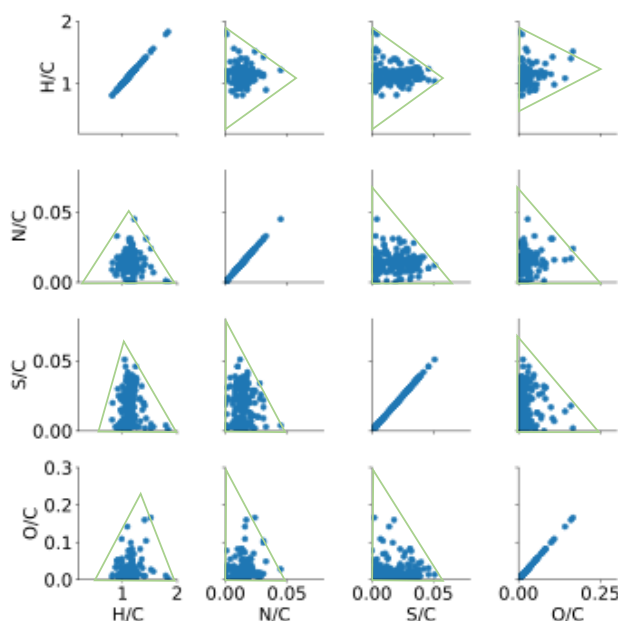


Figure 1: Graphical representation of the methodology adopted to define asphaltenes' pseudo-components. The vertices of the triangles represent pseudo-components and their atomic ratios. The triangles represent the smallest possible ensemble enclosure, therefore, all the samples collected from the literature can be reconstructed as a linear combination of the pseudo-components. Figure gently provided with authors authorization by Guida et al. [6]

The development of the model followed two main steps for each SARA fraction. The first one concerned the formulation of the pseudo-components to generate the surrogate. The pseudo components structure was designed taking advantage of experimental information from literature and in-house experiments performed at King Abdullah University of Science and Technology (KAUST). The second step was the development of the pyrolysis kinetics scheme. The formulation of the kinetic model proceeded through chemistry-related considerations intending to reproduce the all-significant pyrolysis products. Fig.1 represents the graphical approach used to define asphaltenes'

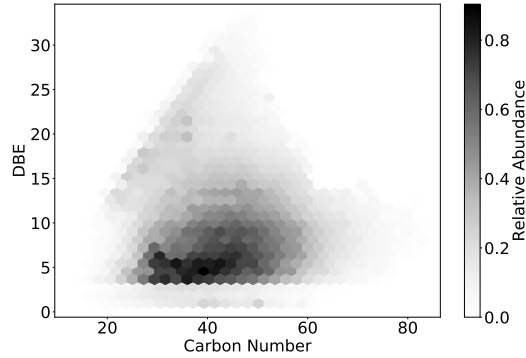


Figure 2: Double Bonds Equivalence vs Carbon number of asphaltenes calculated by FT-ICR MS. Relative abundance is reported as a function of the colour gradient. Figure gently provided with authors authorization by Guida et al. [6]

pseudo-components. The vertices of the triangles represent pseudo-components and their atomic ratios. The triangles represent the smallest possible ensemble enclosure. Therefore, all the samples collected from the literature can be reconstructed as a linear combination of the pseudo-components. Fig.2 reports the double bonds equivalence (DBE) versus carbon number distribution of hydrocarbon molecules in an asphaltene sample. The DBE is an index of molecule aromaticity which identify the number of unsaturations. From Fig.2 is it possible to estimate the average molecular weight and molecular structure fulfilling two of the three objectives reported above. The remaining objective is fulfilled by Fig.1. Merging all this information, is it possible to derive the molecules used as pseudo components for the asphaltenes, and that can be found in the work of Guida et al. [6]. The surrogate for each fraction is then defined as the linear combination of pseudo-components to replicate the fraction's elemental composition. The oil is then reconstructed as the linear combination of the SARA surrogates. Once the pseudo components and the characterization method were designed, the following step was the development of the kinetics scheme. A reaction pathway is associated with each pseudo component. The kinetics scheme was developed to be as simple and general as possible while reasonably accurate. The pyrolytic behaviour of each pseudo component is modelled with a first-order irreversible reaction with the task to approximate the overall kinetics. Each reaction leads to the formation of gas and solid (CHAR) products. Five different solid species were inserted in the model to account for the presence of other atoms in the solid residue. The scheme was tuned following a data interpolation approach. Again further details can be found in the work of Guida et al. [6]. The mechanism for asphaltenes is here reported as an example. The five pseudo components are named progressively from Asph1 to Asph5.

Table 1: Asphaltenes fraction kinetic mechanism. Gently provided with authors authorization by Guida et al. [6]

	A [1/s]	E_a [cal/mol]
Asph 1 \rightarrow 8.62 H_2 + 3 CH_4 + 0.006 C_6H_6 + 0.031 C_7H_8 + 0.01 XYLENE + 0.01 $C_6H_5C_2H_5$ + 0.01 $C_6H_5C_2H_3$ + 0.019 $C_{10}H_7CH_3$ + 56.289 CHAR	5e13	58000
Asph 2 \rightarrow 0.5 H_2 + 4.2 CH_4 + 2 C_2H_4 + 1.843 C_2H_6 + 0.46 C_3H_8 + 0.8 C_3H_6 + 0.276 C_4H_{10} + 0.317 C_4H_8 + 1.068 C_5H_{12} + 1.378 C_5H_{10} + 0.921 C_6H_{14} + 0.987 C_6H_{12} + 0.01 CYC_6H_{12} + 0.36 C_6H_{10} + 0.04 $C_{10}H_{20}$ + 0.003 C_6H_6 + 0.014 C_7H_8 + 0.005 XYLENE + 0.005 $C_6H_5C_2H_5$ + 0.005 $C_6H_5C_2H_3$ + 0.008 $C_{10}H_7CH_3$ + 15.344 CHAR + 1.17 $CHAR_H$	2.5e11	46000
Asph 3 \rightarrow 0.8 H_2S + 0.03 C_8H_6S + CH_4 + 0.9 C_2H_4 + 0.014 C_2H_6 + 0.038 C_3H_8 + 0.924 C_3H_6 + 0.082 C_4H_{10} + 0.8 C_4H_8 + 0.551 C_5H_{12} + 0.394 C_5H_{10} + 0.339 C_6H_{14} + 0.38 C_6H_{12} + 0.075 CYC_6H_{12} + 0.13 C_6H_{10} + 0.083 $C_{10}H_{20}$ + 0.091 C_6H_6 + 0.124 C_7H_8 + 0.42 XYLENE + 0.281 $C_6H_5C_2H_5$ + 0.281 $C_6H_5C_2H_3$ + 0.281 $C_{10}H_7CH_3$ + 17.06 CHAR + 0.148 $CHAR_H$ + 3.17 $CHAR_S$	1e10	41200
Asph 4 \rightarrow 1.5 CO + 2 CO_2 + 2.434 CH_4 + 0.3 C_2H_4 + 1.385 C_2H_6 + 0.292 C_3H_8 + 0.074 C_3H_6 + 0.2 C_4H_{10} + 0.044 C_4H_8 + 0.738 C_5H_{12} + 0.344 C_5H_{10} + 0.639 C_6H_{14} + 0.256 C_6H_{12} + 0.012 CYC_6H_{12} + 0.05 C_6H_{10} + 0.025 $C_{10}H_{20}$ + 0.009 C_6H_6 + 0.044 C_7H_8 + 0.015 XYLENE + 0.015 $C_6H_5C_2H_5$ + 0.015 $C_6H_5C_2H_3$ + 0.026 $C_{10}H_7CH_3$ + 16.21 CHAR + 1.074 $CHAR_H$ + 6.5 $CHAR_O$	2.5e11	46000
Asph 5 \rightarrow 0.04 HCN + 1.22 CH_4 + 0.9 C_2H_4 + 0.832 C_2H_6 + 0.225 C_3H_8 + 0.8 C_3H_6 + 0.098 C_4H_{10} + 0.4 C_4H_8 + 0.798 C_5H_{12} + 0.6134 C_5H_{10} + 0.607 C_6H_{14} + 0.693 C_6H_{12} + 0.065 CYC_6H_{12} + 0.15 C_6H_{10} + 0.012 $C_{10}H_{20}$ + 0.001 C_6H_6 + 0.006 C_7H_8 + 0.002 XYLENE + 0.002 $C_6H_5C_2H_5$ + 0.002 $C_6H_5C_2H_3$ + 0.003 $C_{10}H_7CH_3$ + 23.807 CHAR + 0.515 $CHAR_H$ + 3.96 $CHAR_N$	3e11	48000

As stated before, the complete mechanism comprehensive of surrogates and kinetics scheme formulation for all

the other SARA fractions can be found elsewhere [5].

2.2. Gas phase partial combustion

Gas released during fuel’s pyrolysis is subjected to partial combustion in the gas phase. The kinetics mechanism developed to describe the pyrolysis is merged with a gas phase mechanism to explain partial combustion. Many different mechanisms for the gas phase combustion are available in the literature since kinetic modelling has been a fertile research field for the last century. During selecting the gas phase mechanism, it is possible to define the degree of complexity and the computational cost of the model. This depends on the degree of complexity of the mechanism selected. In this work, the mechanism selected is a reduced version of the AramcoMech 3.0®. This choice was made to keep the model as simple as possible while relatively accurate, to require a very low computational time. Some of the species formed in the pyrolysis step are not present in the gas phase mechanism. To tackle this problem, all the molecules not accounted for in the gas phase were lumped in a similar molecule which is accounted for in the gas phase mechanism. More specifically, paraffin and olefines greater than C4 were lumped in the butene, the most extensive non-aromatic molecule, while aromatics species were lumped into benzene.

2.3. Heterogeneous CHAR gasification reaction

The last step in the formulation of the gasifier kinetic mechanism consists of the heterogeneous gasification of carbonaceous solid residue. For the modelling purpose, only the CHAR accounting for carbon atoms is subjected to gasification. The CHAR reactivity was taken from the literature as global reactions derived empirically from experimental data. Four reactions are used to describe CHAR gasification. The global reactions for CHAR reactivity are reported in Tab.2.

Table 2: Global reactions for CHAR heterogeneous gasification. Kinetics parameters from [7, 8]

	A [1/s]	E_a [cal/mol]
$C + 0.5 O_2 \rightarrow CO$	9e+8	1.28e+4
$C + H_2O \rightarrow CO + H_2$	4e+10	4.28e+4
$C + CO_2 \rightarrow 2 CO$	2.2e+8	5.25e+5
$C + 2 H_2 \rightarrow CH_4$	1.62e+5	6.3e+5

3. Validation

The validation was performed with experimental data related to HFOs gasification reported by Bader [3]. The kinetics mechanism described in the previous section was implemented in ANSYS CHEMKIN R2021® ending in a mechanism with 208 species and 1069 reactions. The thermodynamics properties for the molecules designed as a surrogate for the HFOs were estimated using the group contribution method and empirical correlation as described in section 4 of Brunialti et al.[9]. To initialize the kinetic model the SARA analysis of the HFO is required. Since this information was not reported by Bader et al. [3], the model was initialized with a different HFO sample analyzed in-house and with a similar composition to the one used in the literature. The composition of the two oils is reported in Tab3 together with the SARA analysis and the elemental composition of the fractions. The average molecular weight for Saturates and Aromatics was 500 g/mol and 550 g/mol respectively. Merging all these data the HFO surrogate mixture was defined according to the procedure reported in [5].

Gasifier geometry, pressure, and feed flow-rates are reported in [3, 10]. The gasifier is modelled as a series of two ideal reactors in ANSYS CHEMKIN R2021®. The feed flows into a Perfectly Stirred Reactor (PSR) which is used to model the flame zone immediately after the nozzle. While a Plug Flow Reactor (PFR) is used to model the post-flame zone. PFR length and diameter were set according to geometry data reported by Richter et al.[10]. In his work Richter also reported that the flame at the beginning of the gasifier spread for about one-tenth of the gasifier length. According to this the residence time in the combustion zone (PSR) is one-tenth of the residence time needed to reach the outlet of the PFR. The simulation was set to solve the energy equation and so estimating the PSR temperature and the PFR temperature profile without any external input. Only feed temperature was imposed manually. The steam

Table 3: Elemental composition of HFO sample from Bader et al.[3] and in house analyzed HFO.

	C	H	N	S	O	wt%
HFO from Bader et al.[3]	85.98	10.32	0.63	2.93	0.14	[-]
In-house tested HFO	84.11	10.41	0.12	3.95	1.4	[-]
Saturates	85.30	13.28	0.19	0.1	1.23	35.71
Aromatics	83.05	9.03	0.36	6.46	1.10	40.36
Resins	87.05	8.88	1.14	0.1	2.93	13.02
Asphaltenes	84.13	6.90	0.91	6.32	1.74	10.09

inlet temperature is set equal to the vapour pressure of water at the operating pressure of 60 bar. Oxygen is assumed at ambient temperature and HFO at 60 °C. The HFO temperature is dictated by its high viscosity and it is a common procedure to preheat it to favor the pump work.

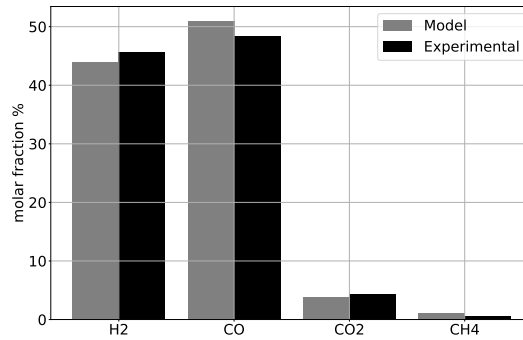


Figure 3: Comparison of experimental data and model results for syngas final composition

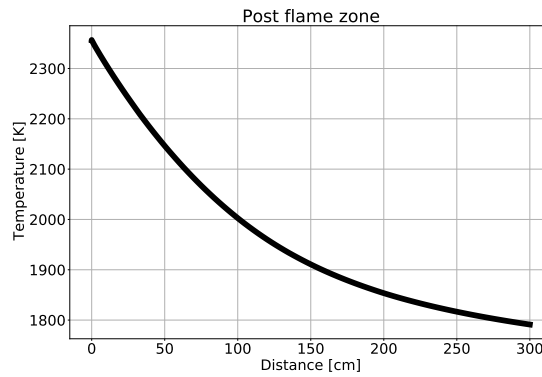


Figure 4: Simulated evolution of temperature along the reactor

The simulations took less than a minute to complete the calculation on a personal laptop. The temperature in the PSR was estimated in 2356 K. The composition obtained by the simulation at the end of the PFR and the one obtained experimentally by Bader et al.[3] are reported in Fig.3. As is it possible to see the agreement between simulation results and experimental data for major gasification products is quite good. Unfortunately, the measurement uncertainty was not reported for the experimental data. Fig.4 reports the temperature profile in the post-flame zone

simulated like a PFR. During the simulation, and according to the experimental data, a heat loss of 50 kW is assumed for the PFR. Despite this, the final temperature from the simulation is 1791 K, slightly higher respect the 1599 K reported by Bader et al.[3]. Probably a more complex scheme for the gas phase partial combustion would lead to a better result, increasing, on the other hand, the computational time required for the simulation.

4. Conclusion

This work proposes a kinetic modelling approach to represent the gasification of heavy and residual oils properly. The model is articulated in three steps: fuel pyrolysis to release gas products and solid carbonaceous residue, partial combustion of pyrolysis gas products, and solid residue gasification. Each of the three steps is modelled with a suitable reaction mechanism. The complete kinetic scheme for heavy oil gasification was obtained by merging the three mechanisms. To model the pyrolysis properly, the fuel has to be represented by a surrogate miming its physical and chemical properties. This work reports a framework for fuel characterization and the definition of a suitable surrogate. The surrogate's formulation is based on data from the literature and in-house performed experiments. The pyrolysis mechanism is then defined from chemical consideration and available experimental data for the oil surrogate. The self-developed mechanism for pyrolysis is then merged into a kinetic scheme able to describe the gas phase partial combustion. Many different tools for gas phase combustion are available in the literature. The selection of the gas phase mechanism defines the degree of complexity and the computational cost of the model. This depends on the degree of complexity of the mechanism selected. In this work, a reduced version of the AramcoMech 3.0® was selected to keep the model as simple as possible while relatively accurate. The final step, solid residue gasification, was modelled according to reactivity available in the literature. The whole kinetics scheme for heavy oil gasification was obtained by merging the mechanism for the three steps of the process.

The model was validated with a studio case available in the literature. Good agreement with the experimental data was obtained for the syngas composition at the end of the gasifier. In contrast, the final temperature at the end of the reactor was slightly overestimated.

The kinetics modelling approach has resulted in a valuable alternative to the too simplistic chemical-equilibrium approach and the too complex CFD modelling, which often requires prohibitive computational costs.

5. Acknowledgments

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