

Integrated Modelling Of Fluid Catalytic Cracking Units

J. Gomez-Prado, N. Zhang, C. Theodoropoulos *

School of Chemical Engineering and Analytical Science,
The University of Manchester, M60 1QD, U.K

In the continuously changing *World of Petroleum*, refiners are under pressure to adjust their product slate and specifications, to work with different types of crude supplies, to meet strict environmental regulations and to switch between different operating policies. Fluid Catalytic Cracking (FCC) units are the most important units in the refining industry, transforming via catalytic cracking heavy crude fractions into more useful and valuable components like diesel, gasoline and light gases. The understanding of the unit behaviour is essential for facing these challenges. In this work we propose an integrated methodology for the modelling of FCCs which includes feedstock characterisation, and riser/stripper/regenerator models that take in account detailed hydrocarbon catalytic cracking kinetics. A modified pivot method is used to feed the characterisation results to the detailed kinetic mechanism developed, which includes lumped species, hence conserving the mass of carbon and of hydrogen. The riser is modelled as a fluidized bed including a 31-lump catalytic cracking kinetic mechanism. The complex gas-particle flow behaviour taking place in the riser section of the unit was modelled using an Eulerian-Eulerian multi-fluid approach implemented in the Fluent computational fluid dynamics package. The influence of linking feedstock characterisation with reaction kinetics as well as the effect of the catalyst distribution profile on the riser's performance is investigated through a number of computational experiments.

Introduction

It is a well-known fact that *light oil* reservoirs are drying out and that the future of the oil industry depends on heavy oil [www.iags.org]. According to this, technologies that transform heavy crude fractions into more useful and valuable components (FCCs, hydrocrackers, etc) will become even more important in the near future. The fact that FCC gasoline represents about 35% of the global gasoline pool [www.world-petroleum.org] and that FCCs are forecast to fill the growing demand of olefins (around 5% per year) [www.uop.com] clearly illustrate the economic importance of FCC units. Therefore, a detailed understanding of the FCC unit behaviour can help refiners to face the challenge of working with heavier feedstocks and new operating policies. Experimental studies are essential for accomplishing such an understanding. However computational tools can offer a complementary more flexible and significantly more cost-effective option for efficiently handling different feedstocks, describing products' quality and for identifying, defining and evaluating operating conditions and policies. We have developed an integrated computational methodology [Gomez-Prado et al, 2006] for the overall modelling of FCC units including feedstock identification; detailed modelling of the riser section involving multi-phase flow dynamics and cracking reaction kinetics and complex interactions between the riser, stripper and regenerator sections.

* Corresponding author: k.theodoropoulos@manchester.ac.uk

Integrated Modelling Methodology

Several approaches can be found in the open literature for the characterisation of refinery feedstocks, as well as different hydrocarbon catalytic cracking kinetic models and also models of the interactions between the different sections of the FCC unit. However, there is a lack of an integrated approach that connects the different FCC modelling aspects. In this work a technique is presented for linking characterisation results to detailed cracking kinetic models and the overall unified method is discussed.

Characterisation methodology

The molecular characterisation of petroleum fractions is extremely difficult since a vast number of components are present in the mixture. Non-experimental approaches for characterisation of hydrocarbon streams typically fall into four categories: 1) pseudo-component-based [Lee and Kesler, 1975], 2) compound class-based [Riazi and Daubert, 1980], 3) average structural parameter-based [Ruzicka, 1983] and 4) representative real component-based [Eckert and Vanek, 2005]. Depending on the information available, different characterisation methods are appropriate for different tasks.

Our compound class approach [Gomez-Prado et al, 2006] (Figure 1) uses a modified Molecular Type Homologous Series (MTHS) matrix [Peng, 1999] to represent paraffinic, naphthenic and aromatic compound fractions, for different boiling ranges (up to 700°C), in hydrocarbon mixtures. The fraction of each component in the stream is estimated by minimising the discrepancies between the bulk characterisation parameters, determined experimentally, and the ones calculated by applying Kay's mixing rule [Kay, 1936] for each cut of the hydrocarbon mixture. The method uses characterisation parameters instead of direct physical properties, because, characterisation factors show better separation ranges between the different homologous hydrocarbon groups [Riazi and Daubert, 1980]. The method was tested against 15 olefin-free petroleum samples, originating from different sources, covering boiling ranges from 120 to 615°C. The results exhibit a maximum relative error of 6.5% [Gomez-Prado et al, 2006], which shows a good agreement with the experimental data.

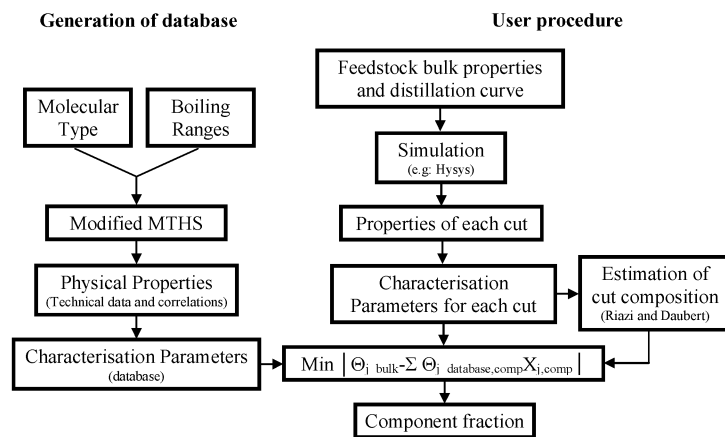


Figure 1. Characterisation methodology

This methodology is important for FCC modelling because it determines the amount of different groups of components present in a stream. This is essential for the accurate simulation not only of the thermodynamic aspects of refinery streams, but also the reaction kinetics of refinery units such as FCCs. Refinery kinetic models are generally

based on lumping schemes, due to the vast number of components present in the feedstocks. In such schemes components are divided into different lumps, according to a representative component which demonstrates the average characteristics of the group. However, this *discretisation* will not always conserve the mass of carbon and hydrogen. Hence, frontier components (species between representative components) need to be distributed between neighbouring lumps. For this purpose, we have developed an approach based on the pivot method [Kumar and Ramkrishna, 1996]. For illustration, if a component of carbon to hydrogen ratio (C/H) α does not fit any of the predefined C/H of the lump representative component, it is divided into two nearest lumps i and j , where $C/H_i < C/H < C/H_j$, with distribution f_i and f_j respectively (see figure 2).

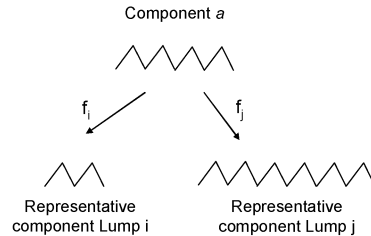


Figure 2. Modified pivot method divides frontier components into the two nearest lumps

The distribution factors (f_i) are calculated via the following linear optimisation:

$$\text{Objective function: } \min (\sum |M.B_i|) \quad (1)$$

$$\text{Where: } M.B_1 = (\sum X_i \cdot C/H_i)_{\text{zone 1}} + (\sum X_i \cdot C/H_i \cdot f_i)_{\text{zone 1-2}} \quad (2)$$

$$M.B_2 = (\sum X_i \cdot C/H_i \cdot (1-f_i))_{\text{zone 1-2}} + (\sum X_i \cdot C/H_i \cdot f_i)_{\text{zone 2-3}} \quad (3)$$

$$M.B_3 = (\sum X_i \cdot C/H_i \cdot (1-f_i))_{\text{zone 2-3}} + (\sum X_i \cdot C/H_i)_{\text{zone 3}} \quad (4)$$

$$\text{Constraints: } X_{\text{lump1}} + X_{\text{lump2}} + X_{\text{lump3}} = \text{Total fraction of family} \quad (5)$$

$$\text{Where: } X_{\text{lump1}} = \sum X_i \cdot \text{zone 1} + (\sum X_i \cdot f_i)_{\text{zone 1-2}} \quad (6)$$

$$X_{\text{lump2}} = (\sum X_i \cdot (1-f_i))_{\text{zone 1-2}} + (\sum X_i \cdot f_i)_{\text{zone 2-3}} \quad (7)$$

$$X_{\text{lump3}} = (\sum X_i \cdot (1-f_i))_{\text{zone 2-3}} + \sum X_i \cdot \text{zone 3} \quad (8)$$

$$\text{Also } 0 \leq f_i \leq 1 \quad (9)$$

Here X_i are the mole fractions of component (cut) i , zone_i is the portion of the lump above or below the characteristic cut, and zone_{i-j} is the combination of two zones belonging to neighbouring lumps between which a component is split.

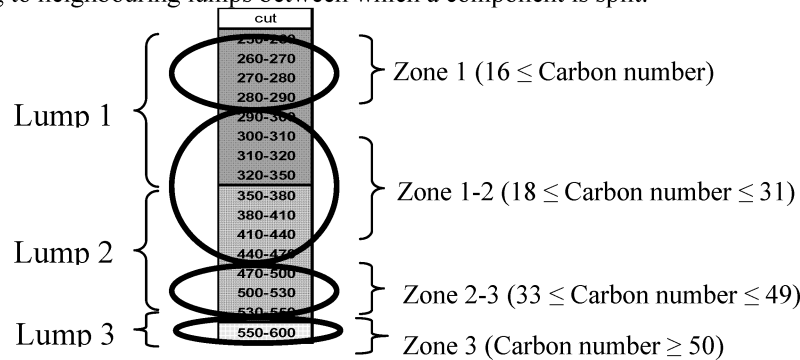


Figure 3. Lumps and zones description

This method will result in a partial redistribution of components into lumps satisfying the carbon, hydrogen mass balances and it can be used for as many lumps as required.

Hydrocarbon catalytic cracking kinetic model

The 31-lump kinetic model [Gomez-Prado et al, 2006] follows the idea of feed-product lumps kinetic approaches, which lump together components behaving in a similar way and treating the resulting components as pseudo-components. The kinetic model fulfils the requirements of the industry, in the sense that it is able to handle different feedstock without having to fit the kinetics and also enables the assessment of product quality (i.e: the amount of components present in gasoline, LPG and dry gas can be computed).

Riser/Stripper/Regenerator model

The riser has been modelled as a 1-D pseudo homogeneous non-isothermal fluidized bed reactor, including the 31-lump kinetic model for catalytic cracking reactions. The catalyst profile is obtained through a 2-D CFD model using the Fluent CFD package, where the complex gas-particle interactions are modelled using an Eulerian-Eulerian multi-fluid approach and the kinetic theory is used to model the viscosity of the solid phase [Chapman and Cowling, 1970; Lun et al, 1994]. For a detailed description of the model for the stripper and the regenerator see Gomez-Prado et al (2006).

Results and Discussion

An industrial hydrocarbon stream, which is feedstock for an industrial FCC unit, was characterised and its components were redistributed to satisfy carbon and hydrogen mass balances for the 31-lump scheme. Two approaches were followed: a simple addition of all components belonging to a specific lump and the modified pivot method (MPM). The results for three lumps can be seen in table 1.

Table 1. Comparison for redistribution of a sample to fit lumped kinetics

	Molar fraction					
	Paraffins		Naphthenes		Aromatics	
	Addition	M.P.M	Addition	M.P.M	Addition	M.P.M
Lump1	0.0128	0.011	0.0057	0.0045	0.0066	0.0086
Lump2	0.344	0.328	0.176	0.1839	0.058	0.0764
Lump3	0.1662	0.184	0.122	0.1153	0.1077	0.0873

In order to compare the MPM with the simple addition simulations were performed using a 1-D pseudo-homogeneous non-isothermal, fluidised-bed reactor using the 31-lump model and a uniform catalyst profile. The results can be seen in table 2. When comparing the results obtained using the MPM to the ones obtained using the addition method (table 2), it can be seen that the MPM produces results closer to the corresponding industrial data. Also, realistically the MPM should be the approach to use, because it is the only one that satisfies mass conservation.

The effect of the catalyst fraction profile on the product yields of a refinery FCC was studied via 1-D simulations of a fluidised-bed pseudo-homogeneous non-isothermal reactor, with 31-lump kinetics. Figure 4 shows the two profiles considered to represent the catalyst fraction profile inside the riser. First, a constant profile which assumes an equal distribution of the catalyst along the riser was assumed, and second, a detailed profile computed using a 2-D gas-solid multi-phase model implemented in the FLUENT CFD package. The results of the simulations and data for the actual industrial unit can be seen in table 3. The results show an improvement on the product yields prediction when a more realistic catalyst profile is used. This improvement is related to the catalyst activity/amount along the riser length. A higher amount of catalyst is present at the beginning of the riser, where the catalyst is still fresh, and a higher concentration of

heavy fractions to crack can be found. The catalyst fraction as well as its activity decreases axially, therefore, products such as gasoline will crack at a lower rate.

Table 2. Comparison between riser product yields using simple addition and the MPM to link feedstock characterisation to kinetics

		Industrial data	Characterisation-Kinetics	
			Addition	MP.M
C2 and lighter	H2	0.01	0.005	0.0061
	CH4	1.1	0.80	0.83
	C2-	0.8	0.45	0.47
	C2=	0.9	0.99	1.06
DRY GAS		2.9	2.24	2.37
C3's	C3-	1.3	0.86	0.96
	C3=	4	5.55	6.1
C4's	i-C4	2.9	1.26	1.43
	n-C4	1	1.97	2.12
	C4=	6.9	6.06	6.49
LPG		16.1	15.69	17.10
Gasoline (C5-221°C)		49.9	45.46	47.59
LCO (221-350 °C)		19	19.09	17.42
DCO (>350°C)		7.2	10.12	8.27
coke		4.9	7.83	7.59

all fraction are in wt%

Table 3. Simulation results using different approaches for catalyst profile calculation

		Industrial data	Catalyst Profile	
			Uniform	Euler-Euler
C2 and lighter	H2	0.01	0.0061	0.0075
	CH4	1.1	0.83	0.83
	C2-	0.8	0.47	0.48
	C2=	0.9	1.06	1.07
DRY GAS		2.9	2.37	2.39
C3's	C3-	1.3	0.96	0.98
	C3=	4	6.1	6.19
C4's	i-C4	2.9	1.43	1.46
	n-C4	1	2.12	2.15
	C4=	6.9	6.49	6.56
LPG		16.1	17.10	17.34
Gasoline (C5-221°C)		49.9	47.59	47.89
LCO (221-350 °C)		19	17.42	17
DCO (>350°C)		7.2	8.27	7.95
coke		4.9	7.59	7.61

all fraction are in wt%

Deviations between the model and the industrial data that can be observed can be attributed to the kinetic model and to the simplifications of the riser model (1D instead of 2D).

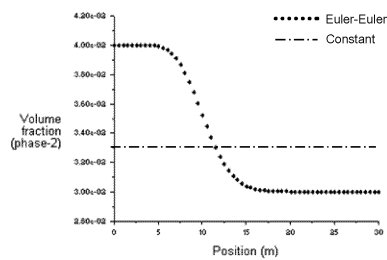


Figure 4. Catalyst profile distributions along reactor length

Conclusions

A methodology for linking characterisation results to a lumped kinetic scheme was presented which allows the transition from the individual components obtained by the characterisation method to the lumped species used by the kinetic scheme satisfying the carbon and hydrogen mass balance. The effects of the catalyst fraction profile on the riser product yield have been shown. As expected, a more realistic profile, computed using a 2-D CFD-based approach, gives closer results to industrial data compared with a constant profile.

References

- <http://www.iags.org/futureofoil.html>
http://www.world-petroleum.org/isc2004/File%20021/134_135_136_138_139_140.pdf
<http://www.uop.com/objects/PetroFCC.pdf>
 Chapan S. and Cowling T., 1970, *The mathematical Theory of Nonuniform Gases*, Cambridge Univ. Press, London.
 Eckert E. and Vanek T., 2005, New Approach to the Characterisation of Petroleum Mixtures Used in the Modelling of Separation Processes, *Comp. Chem. Eng.*, 30, 343
 Feng W., Vynckier E. and Froment G., 1993, Single-event kinetics of catalytic cracking, *Ind. Eng. Chem. Res.*, 32, 2997
 Gomez-Prado J., Zhang N., Theodoropoulos C., 2006, Integrated feedstock characterisation, kinetic modelling and process dynamics for FCC units, 17th International Conference on Chemical and Process Engineering, paper H3.5.
 Kay W., 1936, Density of Hydrocarbon Gases and Vapours at High Temperature and Pressure, *Ind. Eng. Chem.*, Sept. 1014-1019
 Kumar S., and Ramkrishna D., 1996, On the solution of population balance equations by discretisation – I. A fixed pivot technique, *Chem. Eng. Sci.*, 51, 1311
 Lee B. and Kesler M., 1975, A Generalized Thermodynamic Correlation Based on Three Parameter Corresponding States”, *AIChE J.*, 21, 510
 Lung C., Savage S., Jeffrey D. and Chepurnity N., 1994, Kinetic Theories for Granular Flow: Inelastic Particles in Couette Flow and Slightly Inelastic Particles in a General Flow Field, *J. Fluid Mech.*, 140, 223
 Jacob S., Gross B., Voltz S. and Weekman V., 1976, A Lumping and Reaction Scheme for Catalytic Cracking, *AIChE Journal*, 22, 701
 Peng B., “Molecular Modelling of Petroleum Processes”. 1999, UMIST PhD Thesis
 Riazi M., Daubert T. 1980, Prediction of the Composition of Petroleum Fractions, *Ind. Eng. Chem. Process Des. Dev.*, 19, 289
 Ruzicka V., 1983, Estimation of Vapor Pressures by a Group-Contribution Method, *Ind. Eng. Chem. Fundam.*, 22, 266
 Xu Ch., Gao J., Zhao S., Lin Sh., 2005, Correlation between feedstock SARA components and FCC product yields, *Fuel*, 84, 669