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Kinetic Modeling of Vacuum Residue Hydroconversion in a Semi-batch Slurry Reactor.

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Highlights

- A lumped kinetic model is refined for Vacuum Residue Hydroconversion.
- Analysis methods are combined to provide data for the entire boiling range.
- The model is mole based to approach intrinsic reaction kinetics more closely.
- Multiple lumps allow more accurate evolution of residue physical properties.

1. Introduction

Vacuum Residue (VR) consists of very high boiling material, 525+°C, with low diffusivity which leads to mass transfer and coking problems for processing with traditional catalysts. Slurry processes overcome this by using finely dispersed catalysts. Existing models found in the literature use 5 or 6 lumps based on standard refinery cuts and estimate kinetic parameters based on mass fractions [1,2]. The advantage of a mole based model is that it gives a window onto the intrinsic reaction kinetics. However, good estimates of molar masses and volumes are required for both mass and mole balances to be calculated correctly. The challenge is that the heaviest lump has a wide boiling range with no upper limit which leads its composition, and hence its physical properties, to vary during processing. We overcome this by representing the residue in finer detail.

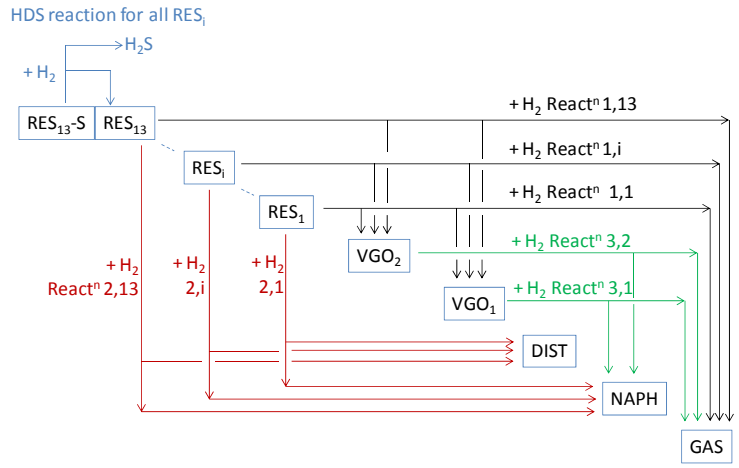
2. Methods

Simulated distillation data, Gel Permeation Chromatography (GPC) and online gas phase analysis results were made available for slurry phase hydroconversion experiments performed with a VR feedstock in a semi-batch reactor at 150 bar and for a range of operating temperatures.

Simulated Distillation (SD) data is quantitative and is therefore the preferred analysis method for petroleum products. However, at the lowest VR conversions, material boiling above 750°C which cannot be measured by SD can amount to 20 wt% of the sample. Riazi's method [4] is a well known technique for SD extrapolation. However, we identified that at low conversions the GPC and SD results have almost identical profiles. GPC is not completely quantitative but has no boiling point limitation. For low conversion VR experiments, the data was therefore combined to produce boiling point curves for the whole of each sample.

Our kinetic model is based on that of Nguyen et al. [3] and is integrated into a validated reactor model which includes vapour-liquid mass transfer. It uses the following lumps: RES (525°C+), VGO (350-525°C), DIST (160-350°C), NAPH (C5-160°C) and GAS (C1-C4). To enable the evolution of the RES and VGO physical properties, 13 smaller lumps are defined within the RES and 2 within the VGO. Their molar masses and molar volumes are found using ProSimPlus 3 with the Grayson Streed thermodynamic model.

The reaction scheme is shown in Figure 1.



$$r_i = \sum_j v_{ij} k_j f_i C_i \; C_{H_2} \qquad (1)$$

$$k_j = k_{0j} e^{-\left(\frac{Ea_j}{RT}\right)} \qquad (2)$$

$$f_i = 1 - e^{-\left(\frac{M_i - M_{i\,VGO2}}{\beta}\right)} \qquad (3)$$

Figure 1. Slurry phase hydroconversion reaction scheme

There are four global reactions: (j=1) RES + H_2 → VGO + GAS, (j=2) RES + H_2 → DIST + NAPH, (j=3) VGO + H_2 → NAPH + GAS and HDS. The reaction rates for each lump, i, are given by Eqn.s (1) – (3) where v_{ij} is the stoichiometric coefficient, f_i is the reactivity which depends on the molar mass, M_i, and the parameter, β and C_i and C_{H_2} are the liquid phase concentrations.

3. Results and discussion

Figure 2 shows parity plots for the smaller RES and VGO lumps for reactions of different duration confirming that a good fit with the data is possible using this method.

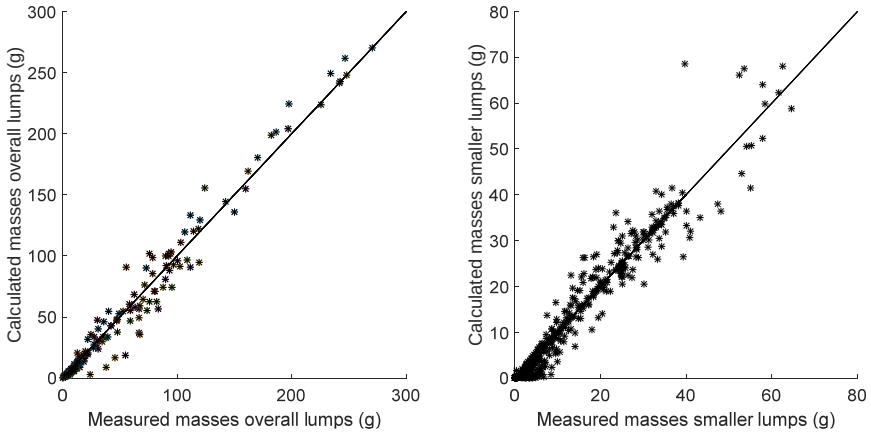


Figure 2. Parity plots for calculated and measured masses of overall lumps and smaller lumps

4. Conclusions

The new approach is effective. The physical properties of the RES evolve with conversion, both mass and mole balances are calculated correctly and a good fit with the data is possible.

References

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Keywords
Slurry phase hydroconversion; Kinetic modeling; Vacuum Residue; Lumped model