

# Predicting reactive heavy oil process operation

## Characterisation of feed and product yields through component structures for better understanding and prediction of operations

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To understand and optimise reactive heavy oil processes encountered in refineries there must be a strong knowledge of the product yields and their physical properties. Sometimes property predictions within models of the reacting material are important due to operational constraints. The coke induction point,<sup>1</sup> or point at which solid coke begins to form in heavy hydrocarbon mixtures, is an example of the importance of property predictions since many unit designs need to take into account solid precipitation if it occurs. The simulation modelling application discussed in this article applies to the Eureka process where fluidisation of reactor materials and inhibiting the coke induction point is essential.<sup>2</sup>

When catalytic or thermal cracking simulation models are developed, enough physics must be encoded into the mathematical development to accommodate for the significant changes in both the normal boiling point of produced material and the associated molecular structures. Many different models for the reactive chemistry mechanisms required to model this class of processes have been proposed. These mechanisms include the use of hydrogen donor components, cyclic ring breaking, dehydrogenation of saturated rings, and cracking versus oligomerised propagation of small to large molecules, to name a few. The required basis for the development of a reliable simulation environment designed to handle the type of detail associated with chemical reaction mechanisms requires

flexible component chemical structures to represent the products from different chemical reaction pathways. In order to capture this type of behaviour directly within the requirements of industrial process simulation software a new PIONA (n-Paraffin, Iso-paraffin, Olefin, Naphthene, and Aromatic) pure component basis environment was developed to both characterise the feedstocks and the resulting products' estimated chemical make-up and yields.

The PIONA technique<sup>3</sup> consists of using constant groups also known as slates of predefined compounds required to cover the carbon number ranges for feeds and products necessary for the modelling of different refinery reactors, such as the Eureka process thermal cracking vessels. The different combinations of these component slates and the compositions of the components within allows for the matching of the experimental distillation curve of a given feed and the calculation of its chemical characteristics, ranging from simple properties such as molecular weight and standard liquid density all the way to more complex physical properties such as heating values, liquid viscosities, and pour points. The key advantage in using this method is its ability to capture the essential chemistry of the feedstock and product mixtures and how the changing compositions upon reaction affect property calculations. The number of components used in the simulation is kept constant and consistency is enforced throughout the simulations.

The PIONA structure group classification was found to introduce an unacceptable property estimation error in studies when modelling feeds with an average carbon number higher than ten, where larger aromatic content was encountered. Further investigation showed that a single aromatic structure group was not enough to differentiate multi-paraffin branched aromatic components against those more reacted compounds that were stripped of straight carbon branches. Therefore, an extra chemical type defined as 'dehydrated aromatic' is included in the PIONA technique.<sup>3</sup> From a molecular structure configuration, these dehydrated aromatics replace branched contributions to a base aromatic ring with additional dehydrated aromatic rings.

### Heavy oil reaction models

Models using detailed specific reaction pathways are commonly found in the technical literature on thermal cracking or pyrolysis of lighter gases such as ethane or even naphtha feedstocks.<sup>4,5</sup> This is possible because the overall number of pure component and radical species are still manageable within a simulation environment (typically less than 150 species), assuming good numerical techniques for the integration of the differential component material and energy balances are employed. Even then, many of these models have to be linearised to help achieve faster computational speeds.<sup>6</sup> Once heavy residual oil feedstocks are introduced, a change in mathematical solution methods for the compo-

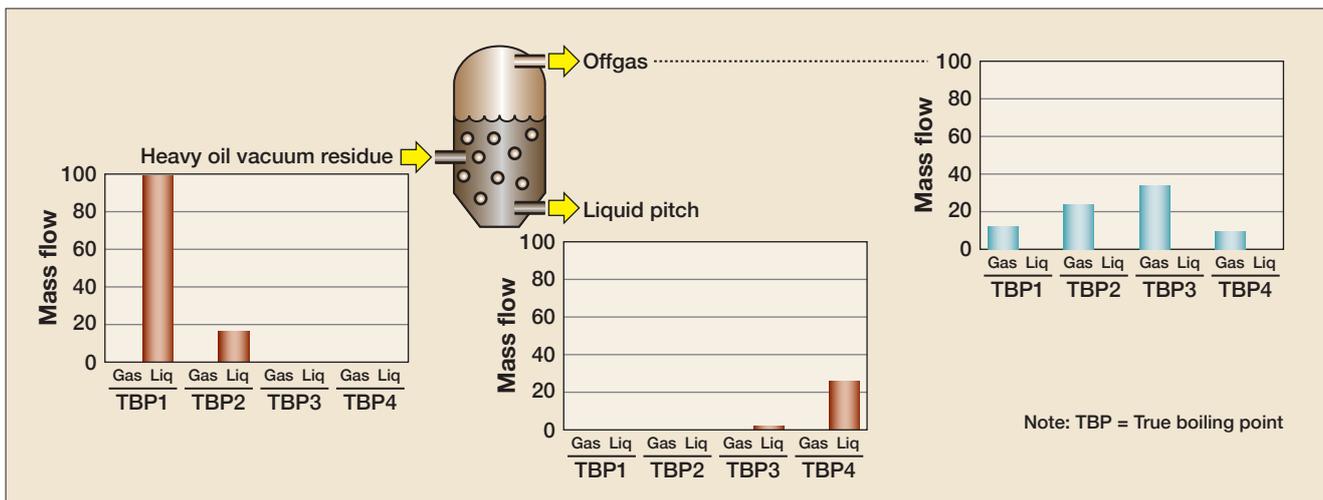


Figure 1 Basic lumped component heavy residue thermal cracking representation

ment material balances is noticed in solutions using generalised, or lumped reaction pathways<sup>7,8</sup> due to the sheer complexity of the feed material. In these models, the heavy residue thermal cracking reactor might use only eight lumped components, a dozen reaction pathways, and resolution of the feed and product material balances would look similar to the representation in **Figure 1**.

This type of modelling relies on the availability of a substantial amount of experimental data which limits the quality of results extrapolated from the model. This lack of predictive power is mainly driven by the non-mechanistic approach to the reaction's kinetic parameter fitting and eventual increase of error outside of the fitted data range. Conversely, this approach

also presents advantages such as fast solution speeds and its ability to predict specific properties of the generalised yield cuts such as the softening point of the pitch and the contained volatile matter<sup>7</sup> through the use of lumped components and effective lumped properties and mixing rules for these properties.

In these lumped models, the resulting temperature profiles calculated for the furnace tubes can also be roughly estimated due to the matched enthalpy of formation for each lumped component, assuming the chemical structure shifts stay consistent and that enthalpies of combustion are available. Significant error would be introduced in these models if hydrogenation versus dehydrogenation occurred since these

reaction pathways are exothermic instead of endothermic. In that respect, average boiling point lumping used by these models is completely non-predictive and would need to be rebuilt for specific processes and eventually even specific plants and equipment.

The PIONA slate technique was applied in the commercial process simulator software VMGSim, to represent multiple hydrocarbon feedstocks in lighter and heavier cut ranges.<sup>3,9</sup> The focus was on property calculations and characterisation of multiple feeds using mixtures based on the same basis component slate. The ability of this PIONA system to model reactive systems is best illustrated in **Figure 2** when compared with the lumped, linearised systems. In **Figure 2**, the

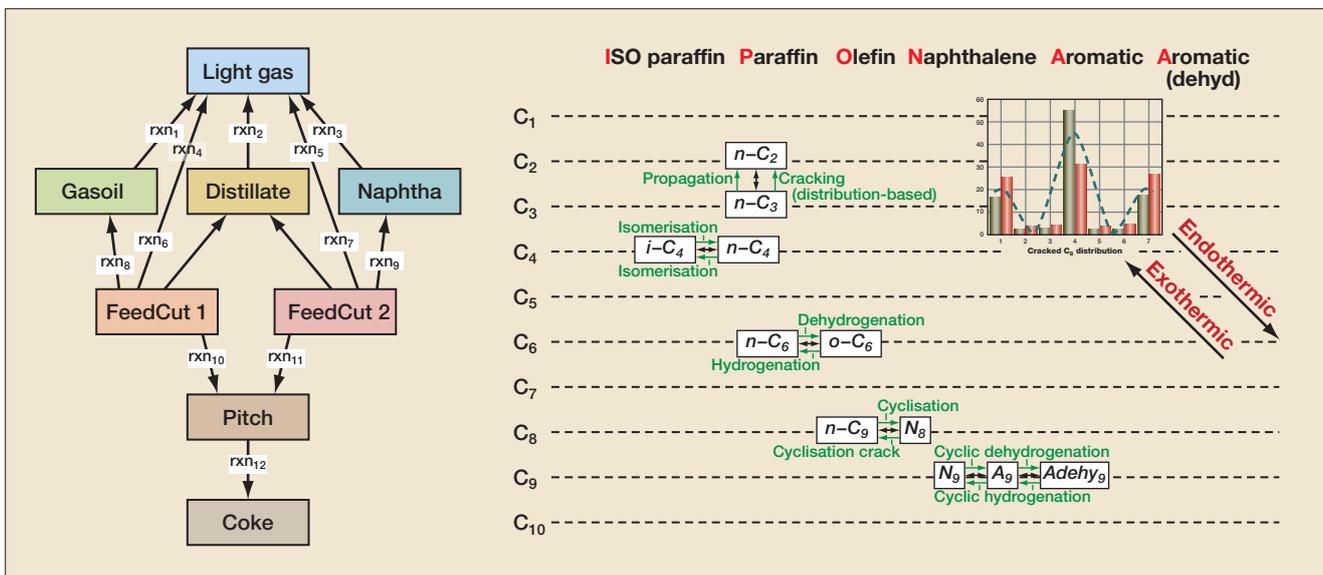


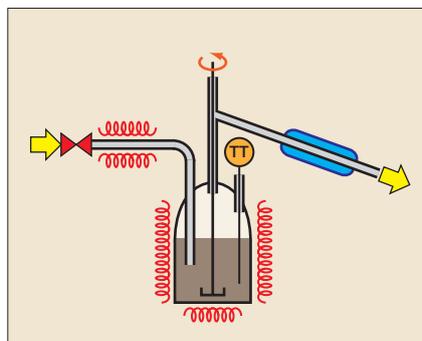
Figure 2 Example of lumped kinetic versus PIONA kinetic thermal cracking reactive pathways

ability to model the transition between carbon number and molecular structure types caused by chemical reactions modelled through reaction pathways is explained as well as the overall heat of reaction effects.

### Characterising process feedstocks and predicting product yields

The key step for the correct modelling of a thermal cracking process such as Eureka is the definition of a correct mixture of PIONA based components needed to characterise the feedstock. Laboratory analysis of hydrocarbon feed material is used to provide the necessary information to fit the model of material stream values against measured properties. The reacted product yields are similarly characterised. The reaction kinetics of the thermal cracking vessel at the desired operating conditions are then simulated and the resulting material product yield's properties and flow rates would be compared to known data. At that point, the process is repeated until the adjustable model parameters are properly defined and the errors between model and experiment are minimised.

The experimental data was gathered through a bench scale batch distillation apparatus shown in **Figure 3**. This bench scale atmospheric thermal boiling/thermal cracking vessel was meant to help understand, characterise, and fine



**Figure 3** Bench scale thermal cracking experimental apparatus

tune the feedstock PIONA composition to be used in the simulation before being used as a basis for the construction of a complete Eureka plant model. The study was done using a Peace River vacuum residue sample representing material from an atmospheric crude tower followed by a vacuum tower in the actual refinery.

The feed sample was introduced to the thermal cracking vessel with the help of a carrier gas and heated to a temperature of 430°C through electric heaters for approximately 45 minutes. An agitator was added within the vessel to minimise temperature gradients, which helped mimic stripping steam introduced to the full scale vessels and the corresponding agitation in actual operation.

**Table 1** shows a comparison between the bench scale experiments and VMGSim simulations for Peace River bitumen feed and

product. **Figure 4** shows how these product cuts' details would look when shown in a similar manner to the simple lumped model represented in **Figure 1**.

### Pour point calculation considerations

The key physical property for the quantification of pitch yield from experimental data included the liquid density, atomic gross analysis, heating value, and pour point of the product. In this case, all properties were important for final pitch product specification, but the pour point is a key indicator to ensure proper fluidisation of the material in the reactor for trouble-free, continuous operation. Typical standard methods to estimate pour points such as ASTM D97 also accepted by the American Petroleum Institute (API), could not be used in a simulation environment due to their inherent limitations. For example, the ranges of the ASTM D97 method's equation are limited to petroleum fractions of 140 to 800 g/gmol and 13 to 50 API gravities<sup>10</sup> and fell short in dealing with ranges of pitch products with molecular weights in the thousands of g/gmol and negative API gravities.

A more rigorous and flexible approach to handle the pour point calculation in the model was devised using viscosity as a correlating parameter. A value of 164 000 cP (164 Pa-s) was selected,

**Peace River bitumen feed and product comparisons**

	Feed	Model <sup>9</sup>	Naphtha	Model <sup>9</sup>	CLO	Model <sup>9</sup>	CHO	Model <sup>9</sup>
API (60/60F)	0.86	0.98	54.5	57.1	30.2	35.8	13.6	14.7
H/C mass ratio	0.115	0.115	0.160	0.165	0.144	0.144	0.127	0.127
Molecular weight	-	1123	-	110	-	178	-	428
	<b>D1160</b>		<b>D86</b>		<b>D86</b>		<b>D1160</b>	
IBP, °C	455	477	57	48	192	194	330	334
10%, °C	-	541	89	100	211	200	368	372
50%, °C	-	716	130	143	250	233	439	458
90%, °C	-	857	162	182	288	301	526	526
FBP, °C	-	892	179	194	310	322	-	569
Iso-Paraffin + n-Paraffin, wt%	-	1.3	46.8	47.0	-	27.9	-	5.0
Olefin, wt%	-	0.0	13.9	14.0	-	12.4	-	5.4
Naphthene, wt%	-	37.2	26.5	24.4	-	26.7	-	42.3
Aromatic, wt%	-	61.5	12.8	14.6	-	33.0	-	47.3
Sulphur, wt%	7.0	7.0	2.8	2.9	4.9	4.9	5.6	5.6

\*CLO = cracked light oil, CHO = cracked heavy oil

**Table 1**

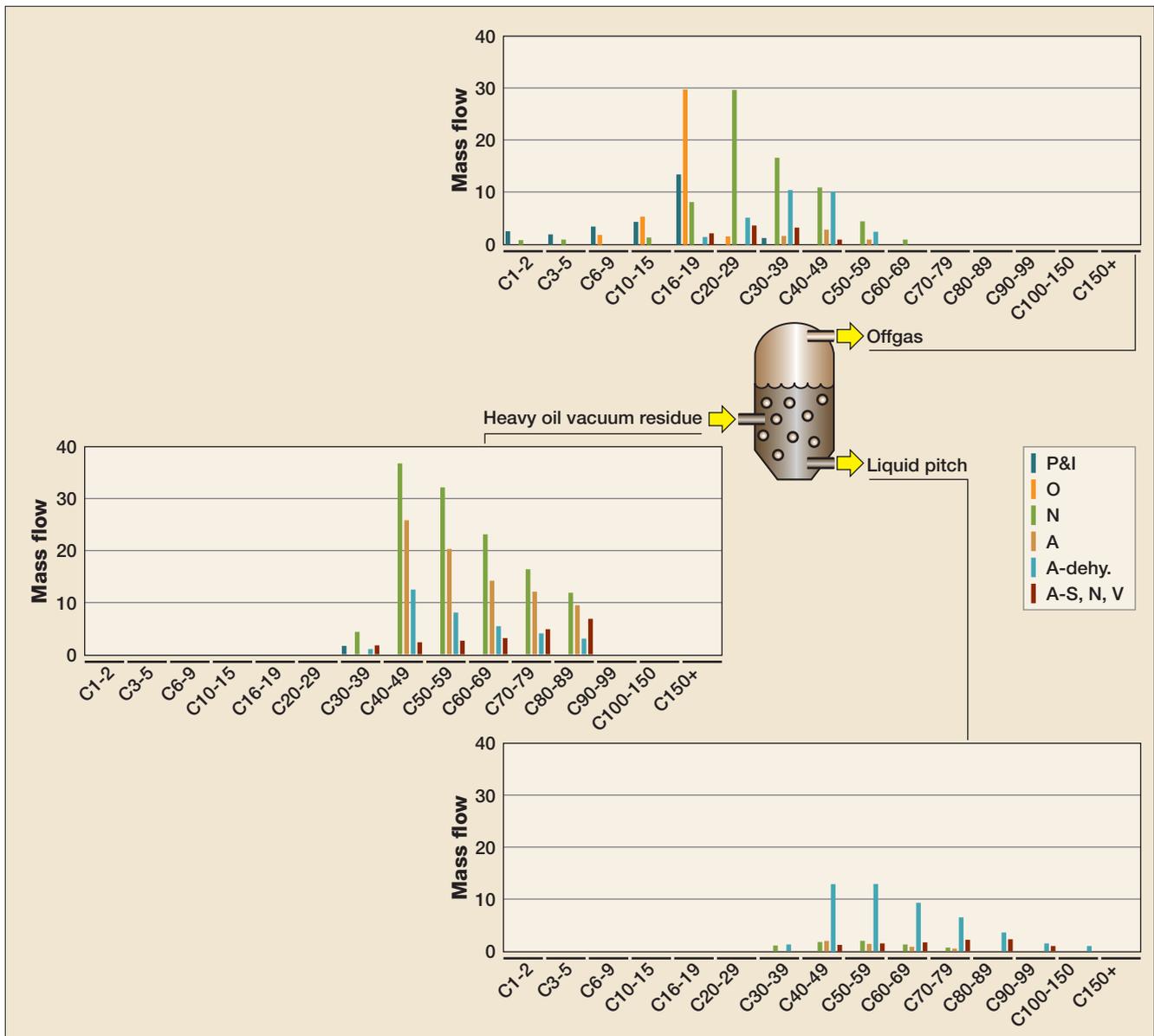


Figure 4 PIONA component slate heavy residue thermal cracking representation

after discussions with heavy oil experimentalists, as a rough equivalent to a pour point based on the observed behaviour of heavy oils and bitumen at ambient temperature. From that reference point a temperature could be found at which the model's pitch viscosity matched and became the estimated pour point temperature. In order to use this type of solution, it would then become important to accurately predict the viscosity of the heavy oil mixtures, also a challenging problem when dealing with heavy hydrocarbon feedstocks.

The viscosity prediction method chosen in the model for the feed and light to heavy product yields was the expanded fluid viscosity model (VMG-EF).<sup>11</sup> The general

principle of this model is that as a fluid expands there are greater distances between molecules and fluidity (inverse of viscosity) of the mixtures increases. The fluidity is assumed to be an exponential function of the expansion of the fluid from a near-solid state. An additional benefit of this method was that binary interaction parameters that model non-idealities due to different molecular sizes and chemical types could be incorporated into the PIONA component slate and characterisation procedure. At the end, the final model was tuned to within a few degrees centigrade to the experimental pour point temperatures together with some actual plant conditions. These results and other resulting

feed and product comparisons of kinematic viscosity are shown in Figure 5.

The Advanced Peng-Robinson property package from VMGSim<sup>9</sup> (VMG-APR) and API correlations (VMG-API) were also used to predict viscosities and are shown in Figure 5. As expected, a correlation like the API based on lighter hydrocarbon mixture data matched experimental data very well for lighter products, but was inadequate when applied to heavier cuts.

#### Application to Eureka process operation

Complete process simulation models were developed once the experimental model's property predictions and reaction kinetics

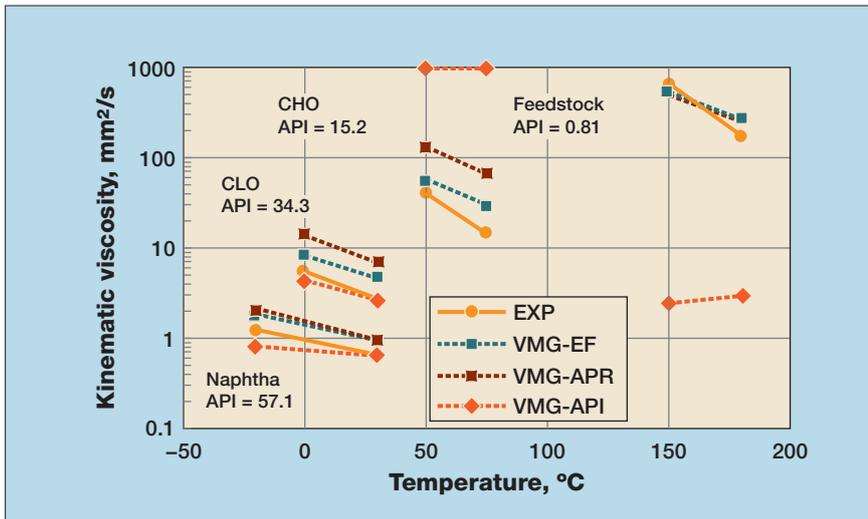


Figure 5 PIONA based kinematic viscosity prediction comparisons

were fine-tuned and validated against the available experimental data. Some of the key points centre on the coke formation trending in the preheating units (not discussed in this article) and operational optimisation like recycle ratio of reacted heavy feed to fresh feed. Figure 6 shows a general Eureka process setup and some of the resulting product yield trends of different bottom recycle oil ratios tested in the model. With the product properties and reacting material pour points being calculated for any point in the operation plant a good overall understanding of new feedstocks outside of previous running conditions was reached.

### Conclusions

Characterisation of a heavy feedstock used in the Eureka reactive heavy oil thermal process was presented based on the use of an extended PIONA and carbon number component slate. This PIONA style simulation model basis was also used for tracking and estimation of hydrocarbon mixture thermodynamic properties before, after, and during reaction. Although solution times were not as fast as with conventional lumped kinetic models (minutes compared to seconds), this model showed flexibility in its more rigorous approach for process situations where structural shifts across

different boiling point ranges could occur.

It was also shown that estimation of focal properties within a PIONA basis simulation, such as the pour point temperature used to monitor the fluidisation inside the vessel, could be estimated with a specially developed empirical correlation, more adequate to heavy feedstocks than available published methods. Estimation methods for properties like viscosity at different temperatures was reviewed with comparisons between the API method and a full range expanded fluid method. The latter allowed for proper temperature dependent viscosity trending when compared with measurements taken from reacted product cut samples.

The model successfully predicted shifts in component representation of feed to reacted products using a PIONA driven reactive kinetic pathway. This more generalised approach still contained all key reaction pathways allowing for the appropriate overall reactive shift to product mixtures in the model, which was further confirmed with resulting accuracy of property prediction comparisons and overall heat of reaction balances. Since the mixture properties calculated were directly tied to the component types and carbon numbers contributions in the model

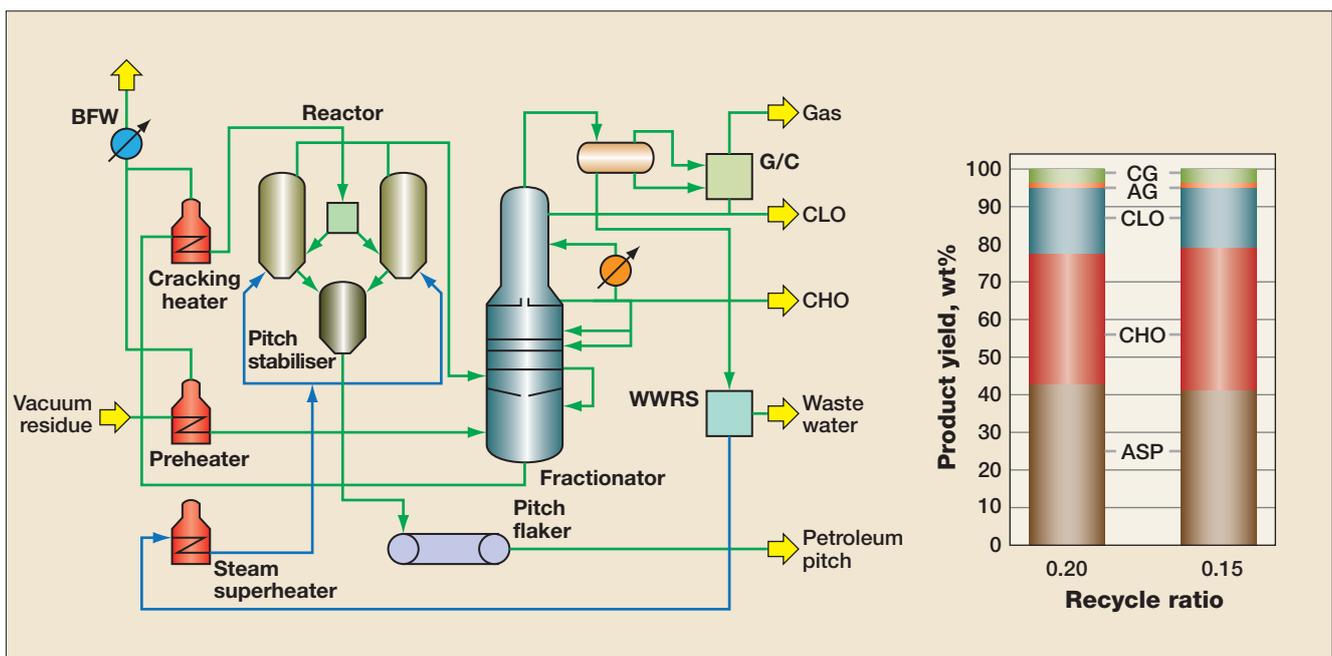


Figure 6 Eureka process and Piece River predicted product yields vs bottom recycle oil ratio

there was accuracy shown in comparisons across a wide range of boiling point temperature product cuts. One could imagine catalyst driven reaction pathways also being potentially modelled using PIONA basis with the reaction kinetic rates properly altered to compensate for catalysed pathways.

VMGSim is a mark of Virtual Materials Group, Inc.

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