

Correlation of processability and reactivity data for residua from bitumen, heavy oils and conventional crudes: Characterization of fractions from super-critical pentane separation as a guide to process selection

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Abstract

Heavier oils are becoming increasingly important as a refinery feedstock. In order to optimize quality and yield of products from the vacuum residues of these intractable feeds, more information on their molecular chemistry is required. Super-critical fluid extraction and fractionation (SFEF) with pentane provides the opportunity to cut deep into the bottoms while readily yielding enough of each fraction to allow characterization and reactivity studies. Results show that problematic species and SARA components (saturates, aromatics, resins and asphaltenes) are asymmetrically distributed among the separated fractions. The determination of average structures based on bulk analysis of the whole residue is heavily biased towards the lighter fractions and provides little information on heavy, difficult to process components. A comparison of bitumen pitch with residues from benchmark crudes, heavy oils and bitumen from non-Athabasca sources, demonstrates that it is not significantly different in its chemical make-up or reactivity to other hydrocarbons. Compared to conventional oils, the intractable nature of bitumen can be largely ascribed to its much higher asphaltene and contaminant contents.

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1. Introduction

As conventional crude production declines, there is an accelerating trend for refineries to process heavier oils and bitumen. Based on economics and infrastructure availability, some bitumen and heavy oil producers upgrade their product on-site to high quality synthetic crude as a premium replacement for conventionally produced oil. In other cases, raw, diluted bitumen or heavy oil, is shipped to central refineries where it is combined with conventional crude oil to produce a blend with a residue content that does not materially impact operations. Current refinery practice utilizes vacuum distillation to remove the bulk of the oil as volatiles, followed

by additional processing to treat a relatively small amount of residue. However, for bitumen or heavy oil, the residuum from straight run distillation is as much as 50% of the original feedstock. This factor, combined with depleting conventional crudes, is compromising the ability to maintain satisfactory blending ratios for optimum operation of some refineries.

At the present time, coking and catalytic hydrogenation are the primary methods for production of higher quality products from residua. Historically, process selection for conventional oils has been evaluated by comparison with benchmark crudes having well-established processability profiles. Typically, simple bulk analysis data, such as H/C ratios, heteroatom concentration, metals and asphaltene contents were sufficient to allow appropriate process choices. While hydroconversion is the technology of choice to avoid coke as a waste by-product, the catalysts involved are easily deactivated, making the process less economically attractive [1]. Also, hydroconversion

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pitch must be disposed of as either coker feed or fuel oil. As the amount of residua increases, processing requirements will become even more challenging and new approaches must be developed and implemented.

As the proportion of bitumen and heavy oil in refinery feedstocks continues to rise, it is necessary for refiners to cut deeper into the bottom of the barrel to optimize the yield of higher value products. This has led to problems in both processing and product quality [2]. In order for the petroleum refining industry to meet these challenges, major changes in operations are needed. It will be necessary to optimize the entire refinery on the basis of compositional process models to achieve the full value from all oil components, particularly the residue fraction [3]. The ability to achieve this objective is strongly affected by the complex chemistry of the residue species [4]. Currently, no standard analytical tool or database is available to provide bottom-of-the-barrel processability data as the basis for future process change [5].

The major issues relating to residua processing are molecular chemistry, metals content, large molecular size and the high carbon content associated with the apparently heavily condensed molecules of the asphaltene fraction. However detailed, the use of bulk analytical techniques for characterization only provides average molecular information. Similarly, standard chemical class analysis, such as SARA (saturates, aromatics, resins and asphaltenes) separation [6] provides another level of detail but yields no particulars about species distribution and molecular size. Some researchers [2] have used chromatographic methods to separate a number of heavy oil residua into as many as 10 chemical class fractions based on acidity, polarity, heteroatom content and aromaticity. Evaluation of fraction reactivity by determination of micro-carbon residue (MCR) and coke composition allowed some generalizations to be made on the partitioning of metals and heteroatoms during coking. However, the limited characterization data did not allow any correlation between molecular structure and process behaviour.

Besides class separations, conventional vacuum distillation to 524 °C, short path vacuum distillation to 700 °C [7] and gel permeation chromatography (GPC) [7,8] are available for hydrocarbon fractionation. While these methods are capable of separating residua on the basis of volatility and molecular size they do not easily produce sufficient quantities of each fraction for the necessary characterization, reactivity and conversion studies. In addition, the high temperature exposure required for vacuum distillation of residua can lead to thermal degradation of samples. However, phase equilibria studies with residua and light hydrocarbons by Peng et al. [9] have led to the development of a super-critical extraction technique for hydrocarbon fractionation suitable for research purposes [10]. Also, work by Sato et al. [11] demonstrated that proper selection of solvent and operating conditions in a super-critical fluid extraction and fractionation (SFEF) system could provide high extraction yields. More recently, this approach has been applied to fractionation of petroleum residua in order to further the characterization and reactivity studies on these samples [4,12].

There are many characterization techniques available for use in structural determination of petroleum components. A recent book by Strausz and Lown [13] details and critically assesses these methods in great detail. Structures for the asphaltene and resin components have also been published [14–18]. However, detailed structural information on heavy hydrocarbons is most easily accessible to researchers through the use of ^1H and ^{13}C nuclear magnetic resonance (NMR) measurements [19–22]. Detailed ^{13}C NMR surveys have been used to determine the molecular parameters for average bitumen molecules, Athabasca bitumen vacuum residuum and their corresponding chemical class fractions [23]. Along with molecular weight and elemental analysis, these parameters provide the basis for the calculation of two-dimensional molecular structures that allow delineation of trends in molecular complexity. However, these simple models do not yield the information on molecular size and conformation required for modelling catalytic reactions. In this regard, the development of computer-aided molecular dynamics (CAMD) presents an important breakthrough in hydrocarbon characterization. This technique, initially used to derive molecular conformations for biological macromolecules and new functional polymers [24,25], has also been applied to the asphaltene component of Athabasca bitumen [26].

Here we discuss recent work on Athabasca oil sands bitumen and its upgraded products incorporating SFEF and SARA separations; a schematic representation of this combination is illustrated in Fig. 1. Characterization of each fraction was accomplished using several advanced techniques with the results providing input to CAMD. The results are correlated with reactivity and conversion studies to provide the basis for recommendations regarding processing approaches for these residues.

2. Super-critical fluid extraction and fractionation

Typical schematics for SFEF separation equipment have been published elsewhere [4,12]. While carbon dioxide is the most frequently used super-critical fluid, it has been demonstrated [12] that light paraffins provide much higher yields during super-critical fractionation of heavy hydrocarbons. Thus, *n*-pentane is the extractant of choice for these

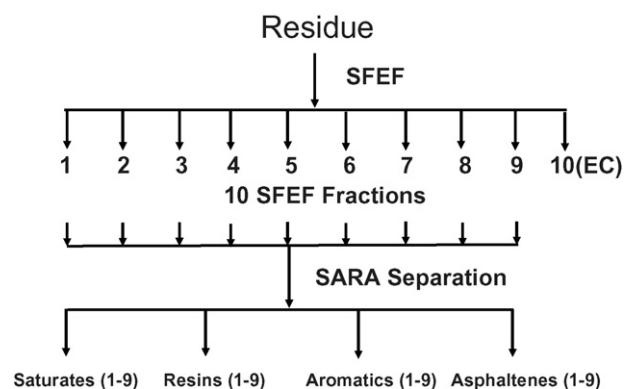


Fig. 1. Schematic representation of combined SFEF and SARA separations. Note: fraction 10 (end-cut) contains most of the asphaltenes; only minor amounts of this component are present in the other 9 SFEF fractions.

separations. Super-critical solvent density is a key operational parameter that is affected by both pressure and temperature. Most stable operation is achieved when temperature, or temperature gradient, in the fractionation column is kept constant, allowing pressure to be used as the primary variable for solubility control. A linear pressure gradient, gradually increased from 4 to 12 MPa over 8 h, slowly raises the solubility of any residuum and provides reproducible results. After extraction, pressure is reduced to evaporate solvent and the sample is collected in a receiver. Recovered solvent is recycled to the solvent reservoir. Any residual, insoluble material, the end-cut, remains in the extraction vessel.

This methodology, developed by the State Key Laboratory of Heavy Oil Processing at the University of Petroleum in Beijing, is capable of producing enough of each fraction for complete characterization and process scale studies. The operation of SFEF is similar to that of vacuum distillation [4] in that it provides fractions of progressively higher molecular weight as the severity of extraction is escalated [27]. The primary advantages are a much deeper cut into the residue and a maximum operating temperature of only 200 °C, much lower than the cracking point of the feedstock [28]. Compared to other techniques, the larger fraction size produced by SFEF allows for SARA type separations on each narrow fraction, providing a detailed distribution of chemical classes as a function of molecular weight. In combination with conversion and reactivity studies on the individual fractions this information provides important input to the selection of upgrading processes for intractable feedstocks.

3. Application of SFEF to residua from conventional crudes

From a processability perspective, crude oils are usually identified as having a paraffinic, naphthenic or asphaltic base. Generally, it is assumed that a residue has the same base as the parent oil and is amenable to processing in an analogous manner. Typically, indices like the universal oil products (UOP) or Watson K factor [29] are derived from empirical data to assess a feedstock and provide a suitable index for quality classification and processability. Crude oils with the same K values have similar bulk properties. For example, the UOP index is defined in Eq. (1) as:

$$K = \frac{\sqrt[3]{T_R^0}}{d_{15.6}^{15.6}} = 1.216 \frac{\sqrt[3]{T_K^0}}{d_{15.6}^{15.6}} \quad (1)$$

where T = average boiling point in °K and $d_{15.6}^{15.6}$ = density at 15.6 °C. The base types are identified as follows: for K values >12.1, the base is paraffinic; when K is between 11.5 and 12.1, the base is intermediate; for K between 10.5 and 11.5, the base is naphthenic, while for $K < 10.5$, the base is asphaltic.

This approach is not generally suitable for naphthenic or asphaltic heavy oils because the Watson K factor is calculated from average boiling points and this information is not readily available for such cases. To overcome the latter deficiency, several attempts have been made to use molecular weight data

to model distillation of high boiling fractions [30–32]. More recent research has applied a group contribution method [33] for the same purpose. Researchers at the University of Petroleum, China have used this approach to confirm that the Watson K factor could not be applied to non-paraffinic heavy oils and residua [28]. They concluded that this failure was attributable to the lack of a parameter representative of chemical composition in the calculation of K .

The same research group carried out additional studies on a number of residues obtained from Chinese and Middle East sources. Samples were selected to include a wide range of chemical compositions. After extensive comparisons between SFEF fractions of the residua [12,28,34–38] a new characterization index, K_H , incorporating H/C ratio, molecular weight and density, was developed as shown in Eq. (2):

$$K_H = 10 \frac{H/C}{M^{0.1236} d} \quad (2)$$

where H/C = atomic ratio of hydrogen to carbon, M = molecular weight (g/mol) and d = density at 20 °C. In this case a $K_H > 7.5$ indicates adaptability to process, $K_H < 6.5$ designates difficult to process while K_H between 6.5 and 7.5 represents an intermediate situation.

Values of K_H for heavy oils and their SFEF fractions correlated well with Conradson Carbon Residue (CCR) values while providing a comprehensive and quantitative measure for their behaviour during thermal cracking and catalytic or pyrolysis conversion [28,34]. A combination of SFEF data and K_H values allows refiners to optimize operations by either cutting deeper into residua bottoms or through selection of the most appropriate process units for different residue fractions. Liu et al. [35] extended this work by using non-linear regression analysis to correlate thermal cracking behaviour and condensation reactions with basic compositional information. Cracking conversion increased not only with H/C ratio but also sulphur and nitrogen contents. Thermal condensation also depended on the ratio of asphaltenes to resins plus aromatics, indicating that coke formation depends on the stability of the colloidal dispersion involving these components.

The earlier work on characterization indices was extended to include Athabasca bitumen pitch and benchmark residua from the Middle East [36]. Analysis of SFEF fractions allowed the distribution of key species to be determined and demonstrated the variation of residue properties for progressively heavier fractions. This important feedstock data allows the refiner to increase yield by tailoring the residua to meet the criteria for a given process unit. In combination with compositional data, the reactivity and conversion studies yielded a modified characterization index K_R as shown in Eq. (3).

$$K_R = 10 \frac{(H/C)^2}{M^{0.1236} \eta^{0.1305}} \quad (3)$$

Here, H/C = atomic ratio of hydrogen to carbon, M = molecular weight (g/mol) and η = viscosity at 70 °C (mPa s). The calculation involves only physical properties and is particularly useful to upstream crude producers. Further research [37] confirmed

the approach and demonstrated that the new index provides a useful assessment of feedstock reactivity and processability. For example, for $K_R < 6$, feedstocks are adaptable to processing, while a $K_R < 4$ is problematic.

For economic and technical considerations, feed selection is extremely important for some refinery processes. For example, residue fluid catalytic coking (RFCC) plays a significant role for conversion of feedstocks low in asphaltene and metals. However, successful operation of this process depends on minimizing the deactivation of catalysts. Regardless, most RFCC operators still rely on commercial experience with benchmark feedstocks and limited pilot plant data [38]. Typically, the resin fraction is the primary source of coke in RFCC processes. The application of SFEF technology to feedstock characterization provides a significant benefit in that it allows the distribution of chemical classes to be determined for heavy oils and residua. This information can then be used to adjust the feed to meet process requirements.

Various hydroconversion processes are also commonly used to upgrade residua. Reactions involving cracking and hydrogenation of hydrocarbons result in the removal of sulphur, nitrogen and other contaminants. A number of studies [38–42] have dealt with narrow distillate fractions from various refining processes. However, information from these studies may not be relevant to residua because their significantly different chemistries require more complex processing steps. In this regard, Yang et al. [43] used the characteristic index K_H described earlier [28] to compare SFEF cuts from several residua of Chinese and Arabian origins. Feedstocks with $K_H < 6$ were found to be associated with high resin and asphaltene contents and were intractable to hydroprocessing. In such cases, sulphur and nitrogen removal approached a constant level comparable to thermal cracking. They concluded that the overall reactivity of residues was dominated by the heavy fractions and that the use of bulk analysis to determine chemistry and reactivity of these feedstocks could be problematic in the assessment of processability.

4. Application of SFEF to bitumen characterization

As mentioned earlier, pitch (524 °C⁺ vacuum residue) represents about 50% of the bitumen feedstock; this material does not respond well to conventional refinery processes. SFEF provides a useful tool for development of the fundamental

knowledge of feedstock and process chemistry required to explain the poor processability of bitumen. Chung et al. [8] used vacuum distillation, followed by SFEF of the vacuum residue, to fractionate atmospheric bitumen pitch and produce multiple narrow front-cuts. The end-cut, amounting to 40% (w/w) of the pitch, was treated as a single fraction comparable to the asphaltene component precipitated by pentane using traditional methods. Compared to conventional crudes and heavy oils, bitumen recovered from mined oil sands has high ash content, amounting to about 1 wt.% of the total extracted bitumen. During fractionation, the ash components concentrate in the insoluble end-cut or asphaltene fraction [44,45]. It has been demonstrated that the ash is largely attributable to organic-coated alumino-silicates that remain strongly associated with bitumen during separation [46]. These solids must be completely removed by ultra-centrifugation to avoid any effect on the quantitative analyses required for characterization of the associated hydrocarbon material [44].

Characterization of the SFEF fractions by vapour pressure osmometry (VPO) measurements shows that separation is based primarily on molecular weight (see Fig. 2(a)). On Fig. 2(b) the values for key properties are plotted against the cumulative weight of fractions prepared from a combination of distillation and SFEF separation techniques. The distributions of these important indicators of processability are clearly asymmetric. However, the continuity of the data suggested that vacuum distillation and SFEF are a good combination for feedstock fractionation. This is not unexpected, as atmospheric equivalent boiling point (AEBP) is known to correlate with molecular weight [47]. Another key feature is the even distribution of carbon and hydrogen up to the 82% cumulative weight fraction point. This observation suggests that molecules in the lighter bitumen fractions have similar basic structures.

The ability of SFEF to readily produce significant amounts of each fraction allows further separation based on compound classes. The normalized SARA distributions in Fig. 3 show that these components are also unevenly allocated among the various fractions. Saturates concentrate with the lighter, front-end samples, aromatic components remain relatively constant, but resin content increases in the heavier fractions. The last fraction, or end-cut, is primarily asphaltic material with only a small contribution from aromatics and resins. Treating bitumen pitch as a *pseudo-fraction* in this way allows evaluation of the contribution from each SFEF fraction to overall processability.

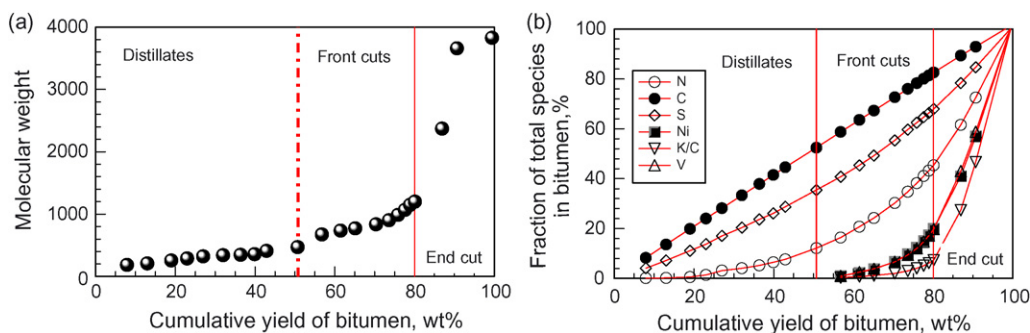


Fig. 2. Distributions of (a) molecular weight and (b) key properties of distillate and SFEF fractions (from: Pet. Sci. Technol., 18 (2000) 587).

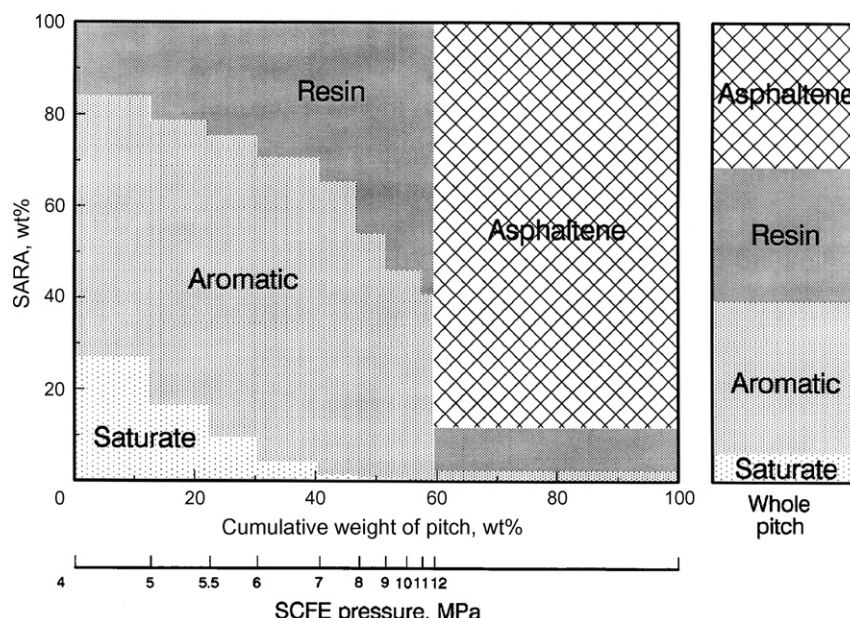


Fig. 3. Distributions of SARA classes among SFEF fractions from bitumen pitch (from: Rev. Process. Chem. Eng., 1 (1998) 41).

As shown in Fig. 4, similar trends were observed in a comparable study on vacuum pitch from Arabian Light benchmark crude. This pitch has more saturates but less aromatics, resins and asphaltenes than the corresponding material from bitumen. Besides the much larger pitch content of bitumen, the major differences between the two samples relate to the asphaltene contents in the original parent oils and their corresponding end-cuts.

Later, Zhao et al. [48] carried out a more detailed characterization study on the same distillation and supercritical extraction fractions described in ref. [8]. Based on solubility in solvent blends of different polarities [49], these researchers also separated the heavy, SFEF end-cut fraction into three parts. In a further refinement, an HPLC technique was used to separate each distillate and SFE fraction into five

compound classes, corresponding to elution times for saturate, mono-aromatic, di-aromatic, poly-aromatic and polar standards (see Fig. 5). Elemental analysis, ^1H and ^{13}C NMR, FTIR spectroscopy and GPC molecular weights provided the basis for determination of molecular parameters for the separated materials. In addition, X-ray photo-electron spectroscopy (XPS) yielded information on sulphur speciation [50]. It was determined that over 80% of saturates in atmospheric topped bitumen pitch are associated with the heavy gas oil distillable fraction. In the heavier SFEF fractions, molecules became more complex with increasing aromatic and heteroatom contents. Although thiophenic and sulphide forms of sulphur occurred in all fractions, the sulphide contents remained relatively constant, while the predominant thiophenic form increased in concentration with component molecular weight. The trend toward more aromatic rings, greater degree of condensation and decreasing degree of ring substitution reached its maximum extent in the three sub-fractions from the end-cut.

As indicated by NMR studies, the predominant molecular features of these heaviest fractions are condensed polyaromatic core structures with high heteroatom (nitrogen and sulphur) and trace metal (nickel and vanadium) contents. Whereas the lightest end-cut sub-fraction is relatively non-polar with molecules containing only 7 aromatic ring structures, the two heavier sub-fractions have more than 10 aromatic rings and are even further enriched with heteroatoms. It was suggested that because these core structures are both coke precursors and powerful chromophores, the visible light absorption measurement might be a good indicator for coking propensity.

In a further development of the work presented in ref. [48], Zhao et al. calculated two-dimensional models for the SFEF fractions [51]. They concluded that any structural analysis, based only on data for the parent residue, would be dominated by the lighter front-cut fractions and the potentially intractable characteristics of the heavy end-cut would not be obvious. For

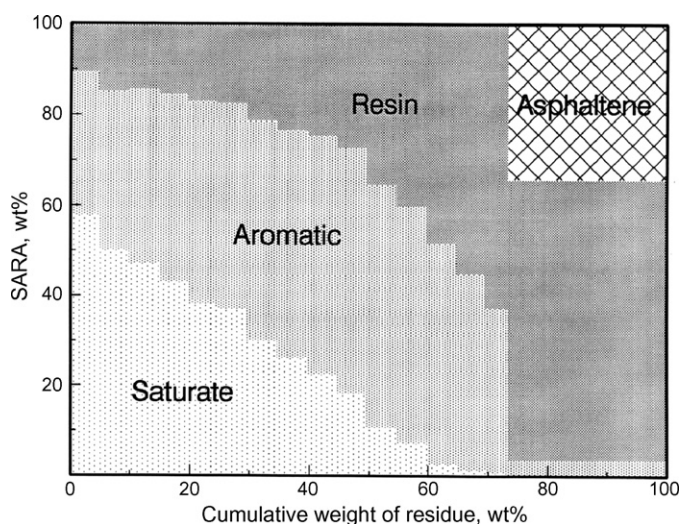


Fig. 4. Distributions of SARA classes among SFEF fractions for vacuum pitch from Arabian light (from: Rev. Process. Chem. Eng., 1 (1998) 41).

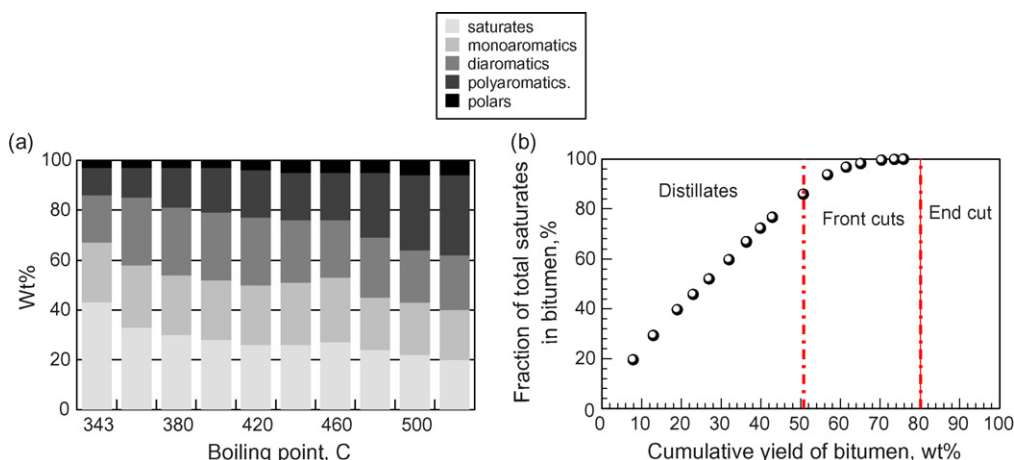


Fig. 5. Distributions of (a) compound classes as a function of distillate fraction mean boiling point and (b) saturates class in narrow-cut fractions (from: *Pet. Sci. Technol.*, 18 (2000) 587).

example, the average pitch structure gave no indication that highly condensed, multi-ring components were present. For the heavier fractions, particularly the end-cut, the NMR data yielded basic unit configurations with molecular weights that did not conform to measured values from either VPO or GPC methods. In fact, the measurement of molecular weight for these types of molecules is somewhat contentious, because the asphaltene fraction, or end-cut, is capable of weak intermolecular association to form micellar-like structures [52]. In fact, recent work [53] using fluorescence measurements indicates that asphaltene molecular weights may be much less than previously thought.

For the basic unit structures derived from NMR, the discrepancy with molecular weights measured by VPO is usually accounted for by assuming that asphaltene molecules comprise several basic units, connected together by covalent aliphatic bridges. For bitumen pitch end-cut, the multiple is about three, a value supported by results from Zhao and Gray [54] who noted a rapid reduction in molecular weight of asphaltene by a similar factor when samples were subjected to rapid thermal

shock. This change did not appear to be associated with major alterations in molecular structure and may have been caused by breakage of inter-unit linkages at weaker $-C-S-C-$ bonds.

Gao et al. [55] applied CAMD to provide more insight into the proposed asphaltene structure. If the individual molecular units are chemically bridged, then the length of the links between the aromatic and hydroaromatic cores is of particular importance. Bridge length plays a key role in governing molecular size and shape owing to the intimate relationship between three-dimensional conformation and total molecular energy. Energy minimisation techniques demonstrated that the optimum bridge lengths should be between five and seven carbon atoms. Using similar materials and methods, Strausz et al. predicted [26] that the probability of bridges with less than three carbon atoms was low. These studies provided clear evidence that simple, two-dimensional models cannot adequately represent the structural, physical or chemical properties of macromolecules.

Building on this foundation, CAMD was used to determine three-dimensional representations of the average molecular

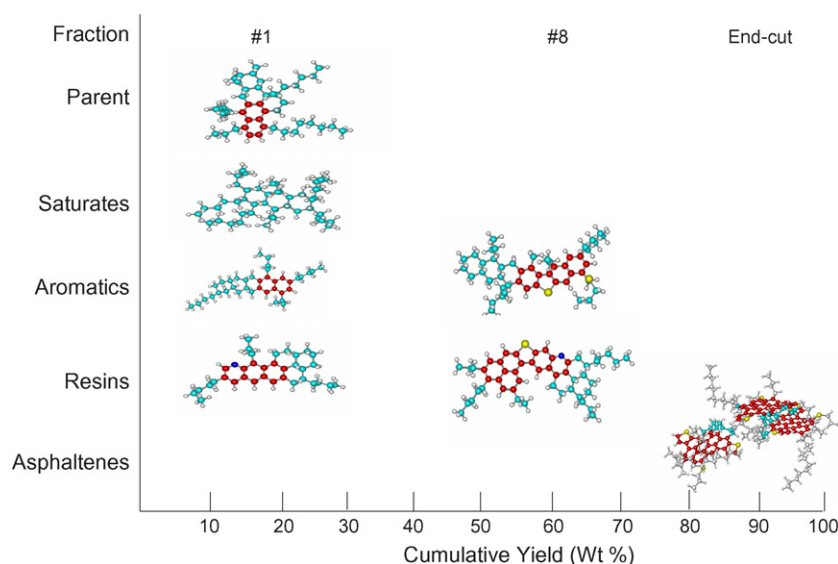


Fig. 6. Three-dimensional structures for solubility classes separated from bitumen narrow-cuts produced by SFEF (from: *Pet. Sci. Technol.*, 21(1/2) (2003) 183).

Table 1

Geometrical characteristics for the lowest energy three-dimensional conformations of SARA fractions (from: *Pet. Sci. Technol.*, 21(1/2), 183–199, 2003)

SFEF fraction number	SARA component	Length (Å)	Width (Å)	Depth (Å)	Eq. diameter (Å)
1	Saturates	15.7	11.2	11.6	16.2
	Aromatic	21.1	10.7	4.1	14.9
	Resin	17.9	10.3	4.5	14.2
	Parent cut	16.2	11.8	11.8	15.7
4	Saturates	nes	nes	nes	nes
	Aromatic	21.9	14.2	7.3	16.4
	Resin	16.5	12.3	6.8	15.1
	Parent cut	21.7	15.9	6.5	16.9
8	Saturates	nes	nes	nes	nes
	Aromatic	19.8	12.7	10.0	16.1
	Resin	24.0	13.6	6.5	15.9
	Parent cut	29.7	10.8	8.5	18.1

nes: Not enough sample.

structures for the SARA classes from the bitumen pitch narrow-cut fractions [27]. Fig. 6 illustrates the differences between the SARA classes from several of the SFEF fractions. The geometrical characteristics of these individual molecules are summarized in Table 1. All classes tended to increase in size with depth of extraction; for the aromatic and resin classes, this corresponded to an increase in number and degree of condensation for the aromatic rings comprising the core of each molecular unit. Another useful observation derived from this work was that nitrogen was heavily concentrated in the resin fractions. In fact, the resins were associated with as much nitrogen as the end-cut, or asphaltene component. Nitrogen functionalities are known to have a negative influence on refining [56,57]. In this regard, it was noted that the MCR of narrow-cut pitch fractions and the corresponding resin and nitrogen contents were nearly linearly correlated (see Fig. 7). The data supports the notion of Andersen and Speight [58] that the resin component is a significant contributor to coke formation during processing. Also shown in Fig. 7 are results from Gray et al. [59] who found that coke deposition on both

catalyst and reactor also correlated well with resin content of the feed during hydroprocessing of these same SFEF narrow-cuts. At the time, little was known about the structures of nitrogen species in resins. However, such information is critical for the development of processes for conversion of these compounds into more tractable nitrogen species. Consequently, these researchers concluded that there is a strong incentive to develop techniques for quantitative nitrogen speciation.

In an attempt to determine whether pitch from Athabasca bitumen is inherently more intractable to processing than other residua, Zhao et al. [60,61] compared molecular properties of comparable components. These included the asphaltene fractions from several different oil sands and SFEF narrow-cuts from benchmark conventional crudes. As seen in Fig. 8, asphaltene from three samples of Athabasca bitumen separated by different methods showed similar, but not identical, average three-dimensional molecular structures. Compared to the asphaltene from bitumen separated by laboratory scale solvent extraction of oil sands, the comparable fraction from commercially extracted bitumen was somewhat less condensed

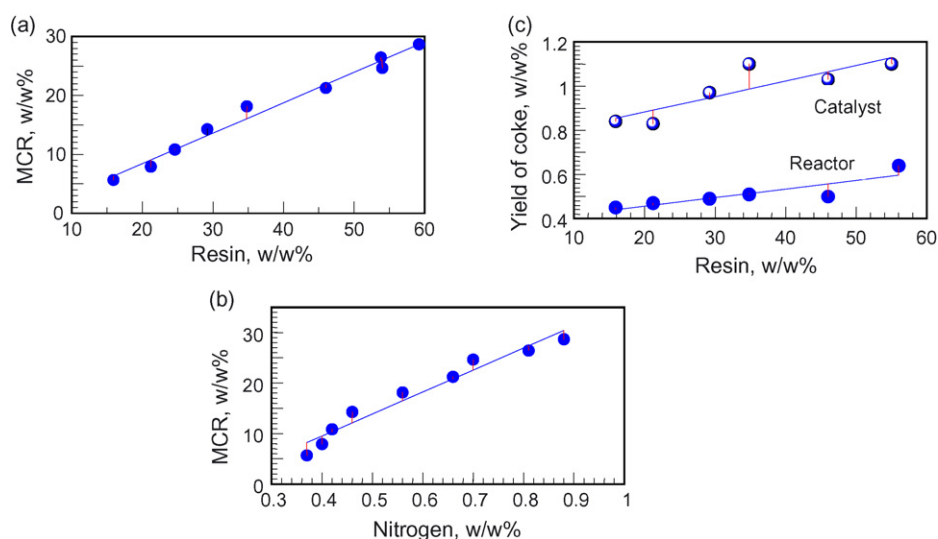


Fig. 7. MCR formation by SFEF narrow-cuts as a function of (a) resin and (b) nitrogen contents of the fractions and (c) coke deposition on catalyst and reactor as a function of resin contents for the same fractions (from: *Pet. Sci. Technol.*, 21(1/2) (2003) 183).

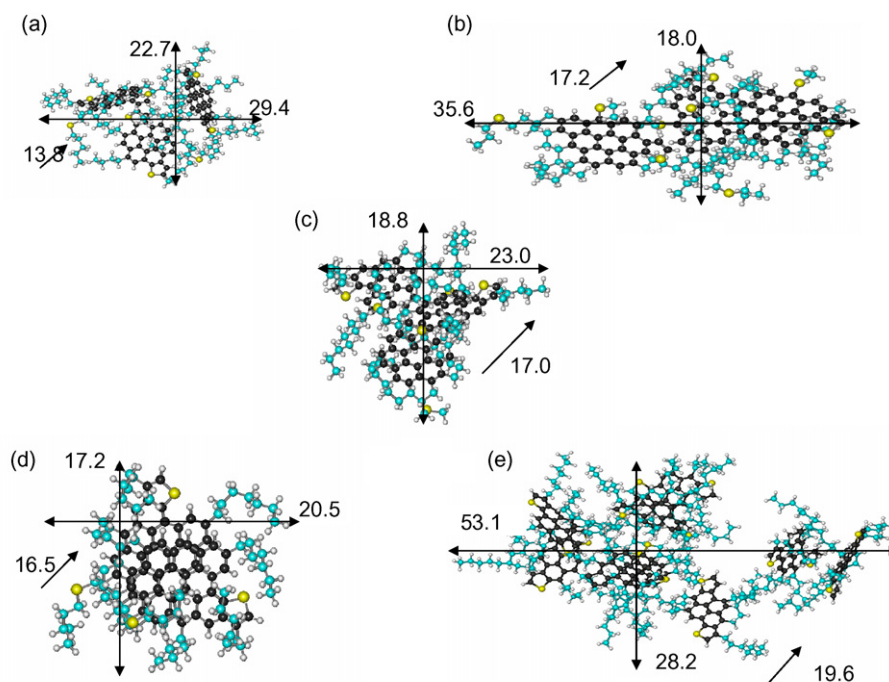


Fig. 8. Three-dimensional conformations of end-cuts (asphaltenes) from different bitumen sources: (a) coker feed bitumen from Athabasca oilsands, (b) bitumen from Athabasca oilsands extracted with toluene, (c) Athabasca bitumen recovered by steam-assisted gravity drainage (SAGD), (d) bitumen from Dahomey oilsands, Nigeria and (e) bitumen from Sunnyside oilsands, Utah, USA (from: Fuel, 80 (2001) 1907).

and substituted. This result indicates that the industrial extraction process does not recover this component in its entirety. Another interesting observation was that a sample from the *in situ* steam-assisted gravity drainage (SAGD) process contained very little entrained solids; such solids usually tend to report with the asphaltene fraction and the much lower concentration of solids in this case suggests that they may be specifically associated with the heaviest fraction of asphaltene. On the other hand, the *in situ* sample contained much higher levels of vanadium and nickel than the asphaltenes from other sources, pointing to either inherent differences between surface and more deeply buried ores or, significant process effects.

Similarly, these same authors also found little difference in the molecular weight, elemental analysis and average structural parameters between pitch from Athabasca bitumen, Venezuelan heavy oil and Arabian light crude [61]. These parallels were highlighted by a striking correspondence between the computed molecular structures, especially their dimensions (see Fig. 9). Considering the large geographic separation of the deposits, the asphaltene fractions exhibited a striking similarity. The computed molecular structures provided no indication that asphaltene from Athabasca sources should be more intractable to upgrading than the corresponding material from other oil sands or conventional crude oils.

However, metals and nitrogen contents for bitumen heavy fractions were much higher than the corresponding values for pitch from the conventional crudes. These elements are among the most intractable in catalytic processing and could have significant adverse impacts on the processes used. It was concluded that complexity of molecular structure is not the

cause of the upgrading problems encountered during processing of bitumen pitch.

5. Processability studies on SFEF bitumen narrow-cuts

In groundbreaking work on bitumen, Chung et al. [8] compared conversion of diluted SFEF pitch fractions by coking, non-catalytic and catalytic hydroconversion processes in a micro-reactor. As shown in Fig. 10, conversion fell roughly into the 50–60% range for each process. Addition of catalyst improved conversion of the heavier extracted fractions by no more than 10%. The end-cut material gave the poorest conversion in each case. Given that reactions were carried out with used commercial catalyst, the similarity in conversion for the three processes was not unexpected. Low catalyst activity would result in domination of residue fraction cracking through thermal chemistry effects. On the other hand, catalysis mediates hydrogenation and heteroatom removal reactions [62,63].

The relatively small decrease in molecular weight of the front-cut fractions after conversion was surprising [64] and indicates that the molecular structure of each fraction is based on similar, relatively large, unreactive cores that are not appreciably changed by increasingly severe processing. Heavier fractions comprise multiples of these core molecules covalently bonded by aliphatic bridges [60,61]. These bridges are easily broken during processing and the common core molecules again dictate the degree of conversion. The presence of catalyst improved sulphur removal from less than 30% to greater than 80% in some fractions. Desulphurisation decreased with increasing molecular weight for each series. This is

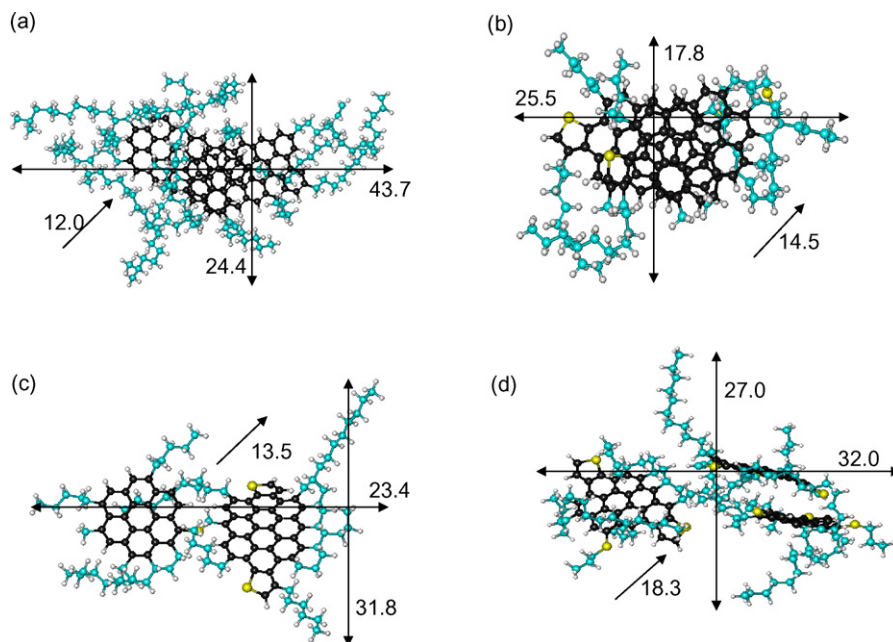


Fig. 9. Three-dimensional conformations of end-cuts (asphaltenes) from different pitch sources: (a) Chinese Daqing, (b) Saudi light crude, (c) Venezuelan heavy oil and (d) Athabasca bitumen (from: Fuel, 8 (2002) 737).

consistent with either declining diffusion rates of increasingly larger molecules within the catalyst pores [63] or higher concentrations of more intractable thiophene sulphur. Hydro-conversion of the diluted end-cut fraction in gas oil over used catalyst was relatively constant, indicating that reaction of this material is predominantly thermal in nature. Values for MCR increased steadily through the series before jumping to 49% for the end-cut. It is normally accepted that MCR values provide a measure of coke yield during thermal processing. According to these authors [8], there was no correlation between coke yields and either MCR or aromaticity for the SFEF fractions. Because the end-cut is most highly enriched in polar species, this fraction is likeliest to undergo phase separation, either as liquid or colloidal solids, leading to the disproportionately higher coke formation observed for this material. In accordance with

other reports [65], a decrease in carbon content of the previously equilibrated catalyst was noted during reaction with each front-cut fraction.

Other researchers [66,67] have postulated that carbon deposition onto catalyst is related to heavy molecule adsorption, dehydrogenation and condensation rather than direct coking [68–70]. The elucidation of this issue is beyond the scope of this work. However, during work with narrow-cuts, it was noted that the fraction having the highest metal and MCR contents was also associated with the largest catalyst carbon content. In this case, mechanisms other than adsorption may lead to catalyst deactivation. For example, metal deposition in pores will also cause pore blockage by promoting dehydrogenation of adsorbed hydrocarbons [59]. Consequently, Chung et al. [8] concluded that it would be more effective to process bitumen pitch fractions separately. While the molecules in the front-cuts become progressively larger and more complex, there is no indication, except in the end-cut, that the associated aromatic rings are more condensed. Thus, the upgrading process for the lighter fractions should be hydrocracking rather than hydrocarbon molecule saturation. The intractable nature of

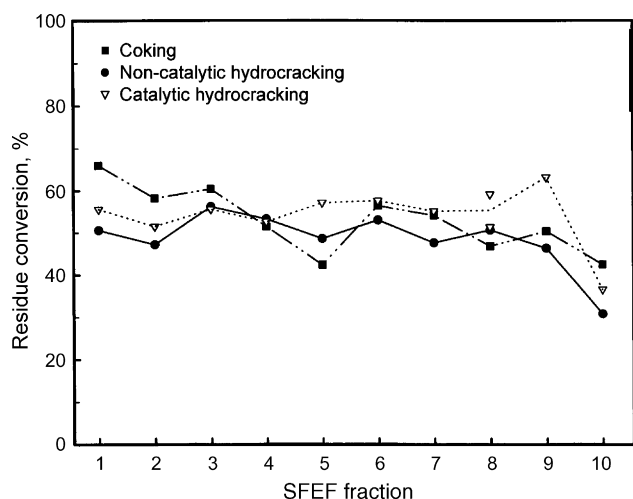


Fig. 10. Conversion of diluted SFE fractions from bitumen pitch under different conditions (from: Rev. Process. Chem. Eng., 1 (1998) 41).

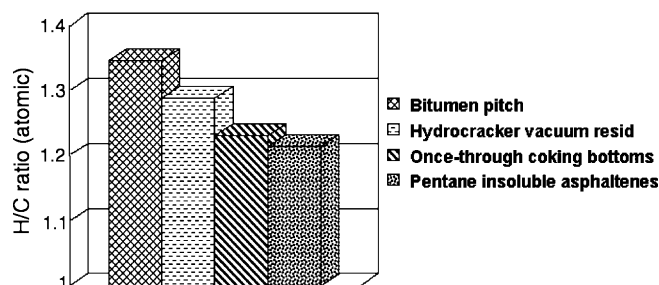


Fig. 11. Hydrogen to carbon ratios for bitumen derived residues (from: Fuel, 80 (2001) 1165).

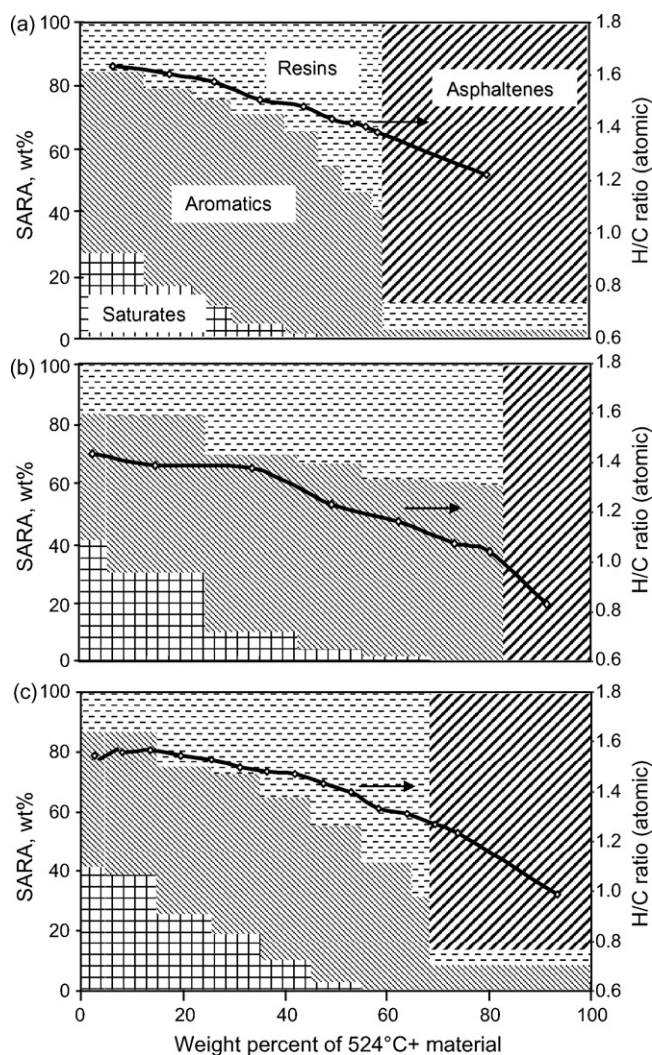


Fig. 12. SARA and H/C ratios for (a) virgin bitumen pitch and residues from (b) once-through coking and (c) catalytic hydrocracking (from: Fuel, 80 (2001) 1165).

bitumen pitch is a result of the high asphaltene content rather than any inherent property of this fraction.

Because the performance of bitumen or residue upgrading processes cannot be predicted using current fundamental knowledge, the design and prediction of coker [69] and hydroconversion performance are based on empirical correla-

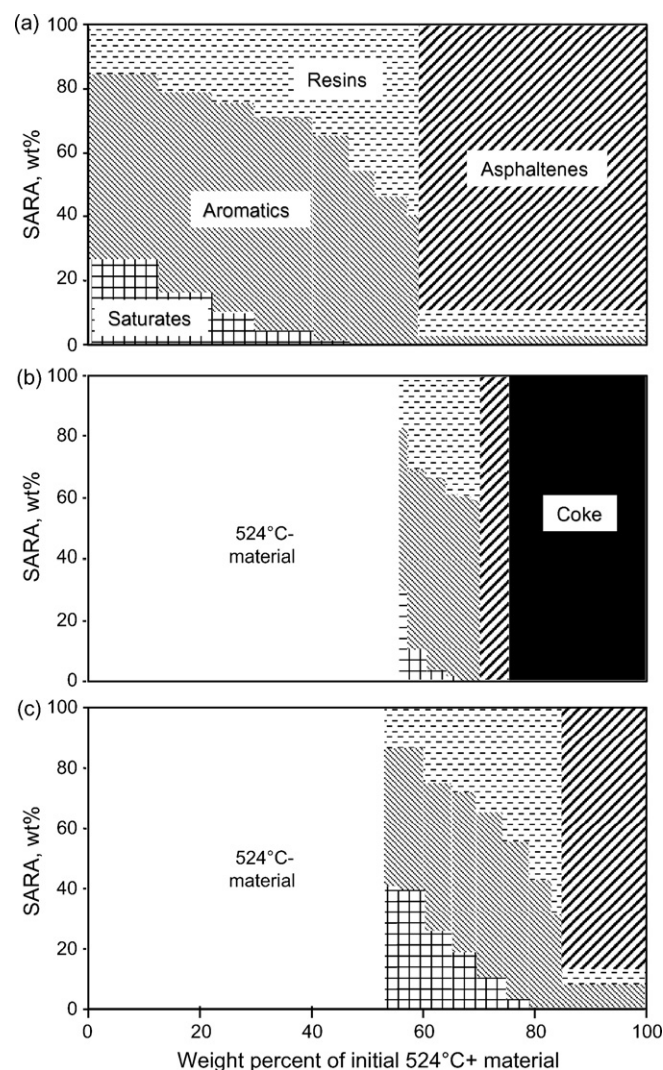


Fig. 13. Distribution of SARA species for (a) virgin bitumen pitch and residues from (b) once-through coking and (c) catalytic hydrocracking (from: Fuel, 80 (2001) 1165).

tions. Such relationships are derived from global changes of bulk species in feed and total product [70–77] and do not represent reactions at the molecular level. As a result, it is not surprising that simple kinetic models are inadequate to fit data from a wide range of operating conditions [74]. Chung and Xu [78] addressed this problem by comparing the quality of

Table 2

Operational pressures and yields for Athabasca virgin bitumen pitch

Fraction number	Pressure (MPa)	Yield (wt.%)	Cumulative yield (wt.%)	Mid-cumulative yield (wt.%)
1	5.0	12.70	12.70	6.35
2	5.5	9.80	22.50	17.60
3	6.0	7.60	30.10	26.30
4	7.0	10.60	40.70	35.40
5	8.0	6.50	47.20	43.95
6	9.0	4.40	51.60	49.40
7	10.0	3.30	54.90	53.25
8	11.0	2.60	57.50	56.20
9	12.0	2.10	59.60	58.55
10 (EC)		40.4		

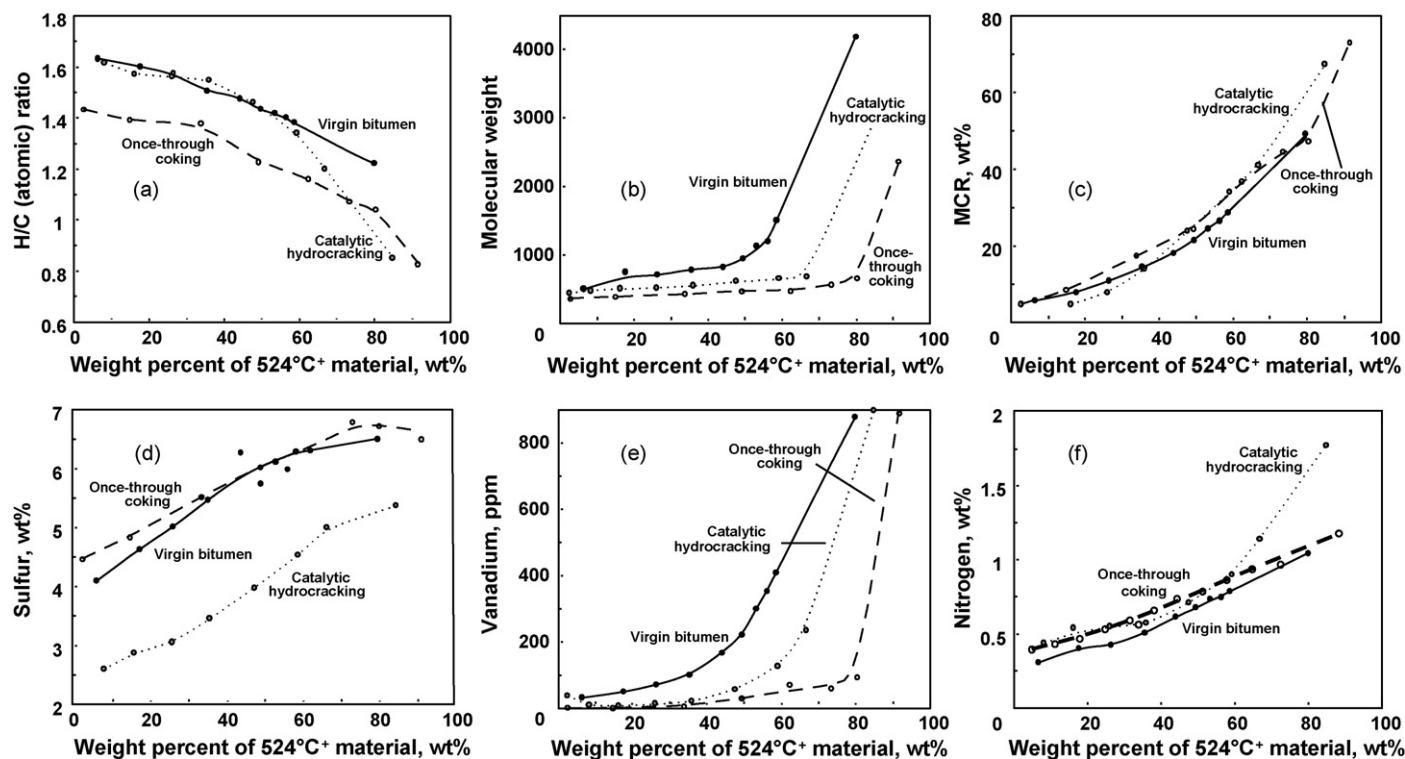


Fig. 14. A comparison of virgin bitumen pitch with residues from once-through coking and catalytic hydrocracking (from: Fuel, 80 (2001) 1165).

residues before and after hydroconversion. As illustrated in Fig. 11, residue quality from hydroconversion is typically lower than that of the feed [77] and deteriorates with increasing process severity. In reality, the process objectives of contaminant removal and increased H/C ratios for the heaviest fractions are not met and the observed overall product improvement is the result of bulk analyses that are biased towards the lighter product fractions.

In their approach, Chung and Xu [78] tracked the transformation of bitumen residue sub-fractions before and after upgrading in order to better elucidate process chemistry. Table 2 illustrates typical SFEF fraction yields; fractions are automatically collected over specific pressure ranges. The amount of each fraction, represented by the bar width in each graph, varies both within and between each residue sample. Based on the results shown in Figs. 12 and 13, these authors concluded that hydroconversion did not upgrade the end-cut fraction and coke formation was merely prolonged through transformation of this material to coke precursors. Partitioning was the common mechanism for removal of key species (MCR, metals and nitrogen) by both hydroconversion and coking. Hydroconversion removed sulphur from the front fractions but not from the end-cut and the distribution of SARA species in the feed and products was different. Based on the results shown in Fig. 14, it was noted that although the MCR values for feed samples and their corresponding products were the same the latter had lower H/C ratios. To explain this observation, they invoked the pendant-core model [78] in which both feed and product fractions contain the same aromatic cores that are the precursors for coke formation.

Zhao et al. [51,79] extended the study of residua from converted bitumen pitch after commercial upgrading operations [76] by determining and comparing the molecular parameters and two-dimensional structures for the various fractions separated by SFEF. In each case, the end-cut fractions from feed and converted samples were studied more extensively by fractionating them into three components based on solubility in solvent blends of different polarities. The average structures for the original residues were compared with a selection of representative front-cuts and the corresponding end-cuts as shown in Fig. 15 [51]. Fractions from the coking residue had lower molecular weights and contained fewer, less condensed aromatic rings than the corresponding fractions from both the original pitch and the hydroconversion residue. Even so, they exhibited lower H/C ratios because of shorter chain, alkyl substituents. Cleavage of alkyl chains at the relatively weaker –C–S–C– bonds occurred more readily during hydroconversion than coking. The predominant (54%) structures present in bitumen pitch are such that they convert to coke or pseudo-solid species when subjected to the thermal treatment encountered during coking or severe hydroconversion. It was concluded [79] that very little of the end-cut fraction from SFEF consists of smaller molecules with aromaticities and polarities low enough to provide useful products after additional processing.

In a comparison of seven diverse conventional and heavy crudes, Tu et al. [80] demonstrated that in terms of coke formation the asphaltene from Athabasca bitumen was less intractable than the equivalent material separated from all other samples except highly paraffinic Chinese Daqing conventional crude. As shown in Fig. 16, coke formation is correlated to well-established molecular parameters, such as

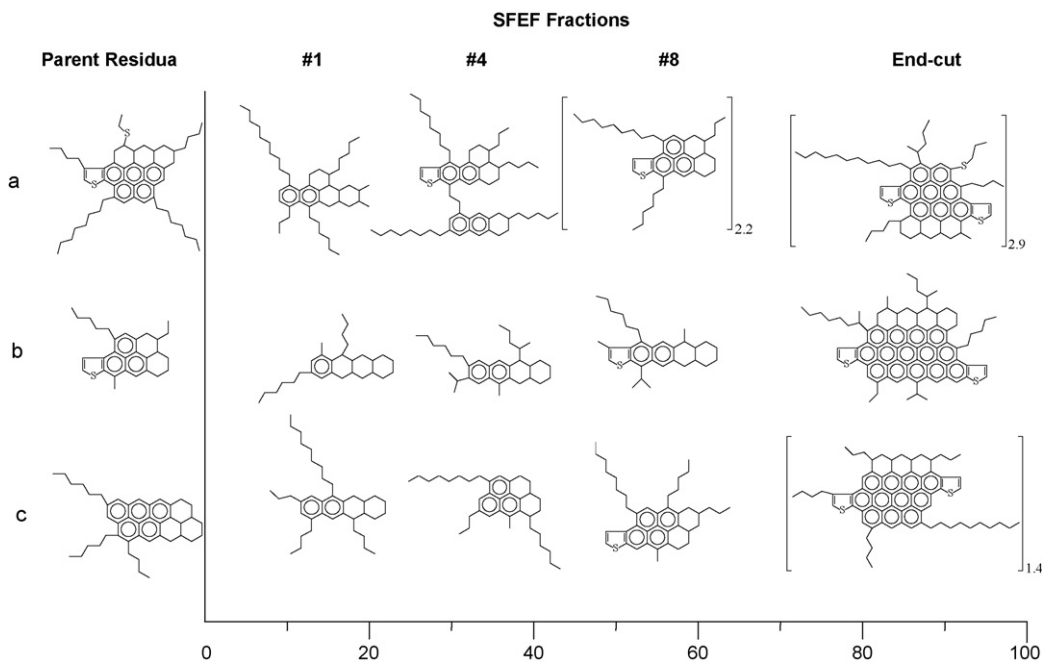


Fig. 15. Average two-dimensional structures for residue, SFE front-cut and end-cut fractions: (a) virgin bitumen pitch, (b) once-through coker residue and (c) hydrocracking residue (from: Energy Fuels, 15(1) (2001) 113).

aromaticity, H/C ratio, molecular weight and side chain length. The asphaltene source appeared to play no role in the response to thermal cracking. These authors concluded that compared to conventional crudes the adverse behaviour encountered during upgrading of Athabasca bitumen is the result of the much higher asphaltene content of the latter material rather than any

inherent property of the asphaltene itself. Although it has been speculated that fine clay minerals, retained in Athabasca bitumen during recovery from surface mined oil sands, could be beneficial in upgrading by providing a catalytic effect, no significant change in conversion was noted in the presence of such solids.

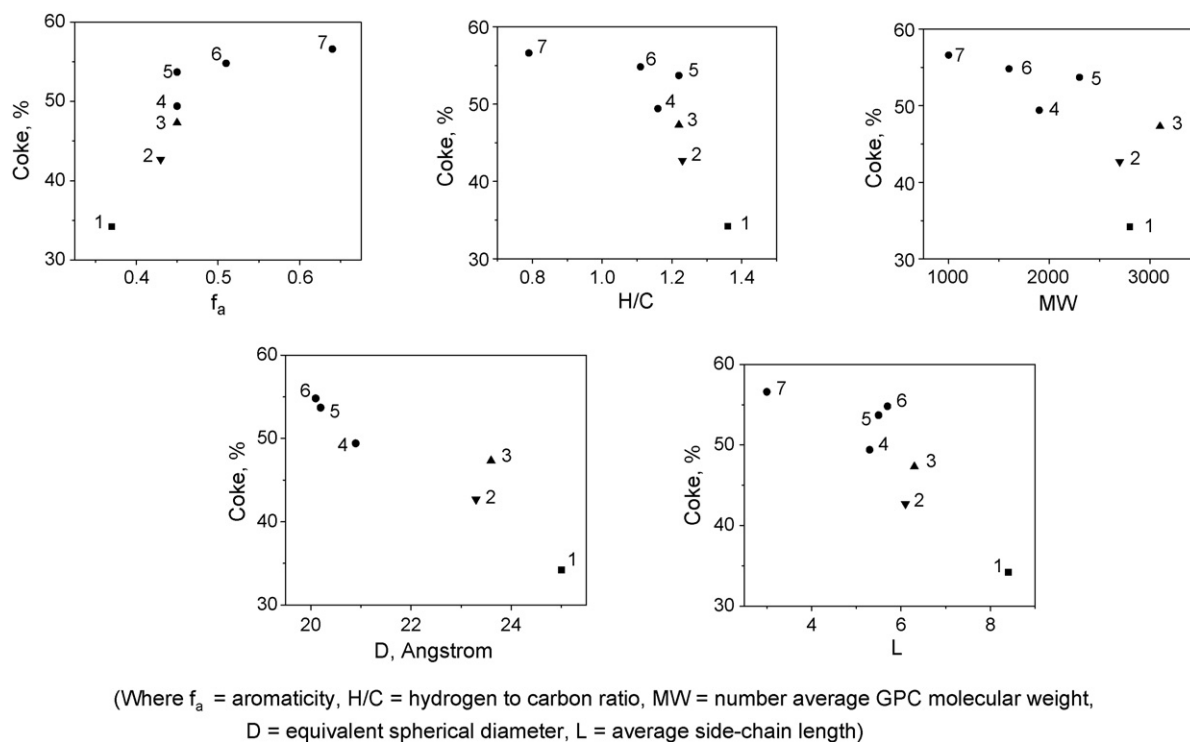


Fig. 16. Coke yields vs. molecular parameters for solids-free pentane insolubles from various sources: (1) end-cut from Daqing crude oil, (2) asphaltene from Athabasca bitumen, (3) end-cut from Athabasca bitumen, (4) end-cut from Venezuelan heavy oil, (5) asphaltene from Nigerian oilsands, (6) end-cut from Arabian crude oil and (7) end-cut from coking residue (from: Pet. Sci. Technol., 24 (2006) 339).

6. Process implications

The findings of the studies reviewed here clearly indicate that prior removal of problematic species is the key step in achieving optimal performance during bitumen processing. In particular, the heaviest, end-cut fraction concentrates asphaltene, metals, MCR and nitrogen; most of the remaining nitrogen is associated with the resin component. High concentrations of these problematic species are known to cause rapid catalyst deactivation.

Emphasis should be on selective separation of the lighter front-cut fractions of bitumen pitch as the primary upgrading process. This would replace the cracking reactions associated with either coking or hydroconversion and allow the remaining bitumen to be transformed into a premium feedstock by conventional refinery processes [8]. Another important observation is related to process selection to treat middle and heavy distillates for product quality and yield improvement. While molecules in these heavier fractions are larger and more complex, there is no evidence that the aromatic rings are more condensed. Thus, the preferred processing route should be hydrocracking rather than hydrocarbon saturation.

Fractionation of residues, or pitches, by SFEF is a useful diagnostic tool for validation of bitumen upgrading processes. Because the solvent polarity in SFEF is readily controllable this technique also offers the most flexible approach to bitumen pitch separation. Recent work on high-pressure phase behaviour involving residua and light hydrocarbons [81,82] is being used to optimize the technique, conceivably leading to a process capable of yielding several fractions that can be treated separately by the most appropriate means. The majority of the SFEF end-cut fraction does not yield useful products and should rather be considered as a potential feed for gasification or as a source of value-added products.

7. Conclusions

Major changes in operations will be needed to enable the petroleum refining industry to meet the challenges posed by residue processing. It will be necessary to optimize the entire refinery on the basis of compositional process models to achieve the full value from all feedstock components. Current reliance on bulk analysis is shown to give an overly optimistic picture of reactivity. Also, typical processability indices, derived for benchmark crudes, are not applicable to most residues. While specific, empirical indices can be derived for these feedstocks they still provide only general guidelines to chemical reactivity.

Super-critical fluid extraction allows deep fractionation of residues without subjecting the samples to the high temperatures associated with distillation. The technique also readily provides enough material for detailed characterization and reactivity studies. Comparisons between residues from different sources show only minor differences in composition. The lighter, distilled fractions and deeper super-critical material from the same residue show a continuity of property trends, indicating that both separations are based primarily on molecular weight.

Analytical data shows an asymmetric distribution for most molecular properties and SARA classes. However, an even distribution of carbon and hydrogen through the distilled and extracted front-fractions suggests a similar basic structure in these samples. In terms of the SARA components, about 80% of saturates occur in the distillable fraction of pitch, aromatic contents are relatively consistent in all fractions while the amount of resin increases with molecular weight.

Molecules in the heavier fractions are more complex with increasing aromatic and heteroatom contents. In particular, thiophenic sulphur content increases with fraction molecular weight. Data from NMR shows a trend for increasing number of aromatic rings and degree of condensation, combined with decreasing ring substitution, reaching its maximum extent in the insoluble end-cut. About half of this fraction is relatively non-polar with cores containing only seven aromatic ring structures. The remaining end-cut is associated with cores containing at least 10 rings and is more heavily enriched in nickel, vanadium and nitrogen. The resin fraction is the reservoir for nearly 50% of the total nitrogen content. Correlation with MCR data indicates that nitrogen species are also a significant contributor to coke formation.

There was little difference in response of SFEF fractions to conversion by coking, non-catalytic and catalytic hydroconversion processes. Except for the end-cut, conversion was between 50 and 60% in each case. The addition of used commercial catalyst produced a 10% improvement for the heavier material. The relative insensitivity of fraction conversion by the different processes seems surprising but may be the result of low activity of the catalyst used in these tests. However, the fact that conversion produced relatively little molecular weight reduction for the lighter fractions indicates that the molecular structure and reactivity of each fraction is similar in each case. Relatively large and unreactive core molecules must dominate these structures so that increasingly severe processing has little effect on molecular weight. Heavier fractions comprise multiples of the core molecules joined by aliphatic bridges. The sulphide linkages in these bridges are easily broken during processing and the common core molecules again dictate the degree of conversion. While catalyst use improved desulphurisation from 30 to 80%, its effectiveness declined for the deeper cuts. There was no correlation between MCR and coke yield for bitumen pitch fractions.

Hydroconversion residues are of lower quality than the feed and generally deteriorate further with greater process severity, i.e., the process objectives of higher H/C ratios and contaminant removal from the heaviest fractions is not met. In this respect, a comparison of SFEF fractions before and after hydroconversion showed that coke formation by the end-cut is not reduced but merely prolonged. Similarly, sulphur is removed from the front-fractions but not the end-cut. Results from H/C and MCR measurements indicate that feed samples and their corresponding products contain the same aromatic cores. Only part of the end-cut comprises smaller molecules capable of being processed to useful products.

Conversion of asphaltene from different sources is not noticeably different. This demonstrates that the problems with

Athabasca bitumen processing are not caused by the asphaltene fraction *per se*, but rather the much larger amount of this component present in the feedstock.

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References

- [1] J.M. Oelderik, S.T. Sie, D. Bode, *Appl. Catal.* 47 (1989) 1.
- [2] J.B. Green, G.P. Sturm, J.Y. Shay, J.A. Green, J.W. Reynolds, L.L. Young, J.S. Thomson, *Proc. Symp. on Exploration Characterization and Utilization of California Heavy Fossil Fuel Resources*, San Francisco, 5–10 April, Am. Chem. Soc., Div. Petrol. Chem. 1992.
- [3] J.P. Katzer, M.P. Ramage, A.V. Sapre, *Chem. Eng. Prog.* (July) (2000).
- [4] K.H. Chung, C. Xu, Y. Hu, R. Wang, *Oil Gas J.* 95 (January (3)) (1997) 66.
- [5] F.S.-C. Lee, *Am. Chem. Soc., Div. Fuel Chem.* 40 (3) (1995) 497.
- [6] E. Lundanes, T. Greibrokk, *J. High Res. Chrom.* 17 (1994) 197.
- [7] E. Furimsky, P.J. Champagne, *Fuel Process. Technol.* 6 (1982) 269.
- [8] K.H. Chung, C. Xu, M.R. Gray, Y. Zhao, L.S. Kotlyar, B.D. Sparks, *Rev. Proc. Chem. Eng.* 1 (1998) 41.
- [9] C.L. Peng, R.A. Wang, Y.H. Fan, G.H. Yang, *Proc. 1st Int. Symp. Supercritical Fluids*, Nice, France, (1988), p. 829.
- [10] G.H. Yang, Y.H. Fan, R.A. Wang, S.-S. Jia, *Proc. Int. Conf. Petroleum Refining and Petrochemical Processing*, Beijing, China, (1991), p. 201.
- [11] M. Sato, M. Goto, T. Hirose, *Ind. Eng. Chem. Res.* 35 (2) (1996) 37.
- [12] T.P. Shi, Y.X. Hu, Z.M. Xu, T. Su, R.A. Wang, *Ind. Eng. Chem. Res.* 36 (1997) 3988.
- [13] O.P. Strausz, E.M. Lown, *The Chemistry of Alberta Oil Sands, Bitumens and Heavy Oils*, Alberta Energy Research Institute, Calgary, 2003.
- [14] O.P. Strausz, T.W. Mojelsky, E.M. Lown, *Fuel* 71 (1992) 1355.
- [15] J. Murgich, J. Rodriguez, Y. Aray, *Energy Fuels* 10 (1996) 68.
- [16] O.P. Strausz, T.W. Mojelsky, E.M. Lown, *Energy Fuels* 13 (1999) 228.
- [17] J. Murgich, J.A. Abanero, *Energy Fuels* 13 (1999) 278.
- [18] J. Murgich, O.P. Strausz, *Pet. Sci. Technol.* 19 (2001) 231.
- [19] J.G. Speight, *Fuel* 49 (1970) 76.
- [20] J.G. Speight, *Fuel* 50 (1971) 102.
- [21] Y. Takagami, Y. Watanabe, T. Mitsudo, M. Itoh, *Fuel* 59 (1980) 253.
- [22] T. Susuki, M. Itoh, Y. Takegami, Y. Watanabe, *Fuel* 61 (1982) 402.
- [23] L.S. Kotlyar, J.A. Ripmeester, B.D. Sparks, J.R. Woods, *Fuel* 67 (1988) 1529.
- [24] L.C. Brooks, M. Karplus, B.M. Pettit, *Proteins: A Theoretical Perspective of Dynamics, Structure and Thermodynamics*, J. Wiley, New York, 1988.
- [25] C.R.A. Catlow, in: C.R.A. Catlow, S. Parker, M. Allen (Eds.), *Computer Modelling of Fluids, Polymers and Solids*, NATO ASI Series, vol. 293, Kluwer Academic, 1990.
- [26] O.P. Strausz, T.W. Mojelsky, E.M. Lown, I. Kowalewski, F. Behar, *Energy Fuels* 13 (1999) 228.
- [27] S. Zhao, L.S. Kotlyar, J.R. Woods, B.D. Sparks, J. Gao, K.H. Chung, *Pet. Sci. Technol.* 21 (1/2) (2003) 183.
- [28] T.P. Shi, Z.M. Xu, M. Cheng, Y.X. Hu, R.A. Wang, *Energy Fuels* 13 (4) (1999) 871.
- [29] K.M. Watson, E.F. Nelson, *Ind. Eng. Chem. Res.* 25 (8) (1986) 880.
- [30] K.S. Pedersen, A. Fredenslund, P. Thomassen, *Properties of Oils and Natural Gases*, Gulf Publishing Co., Houston, 1989.
- [31] M.R. Riazi, T.E. Daubert, *Hydrocarbon Process.* 59 (3) (1980) 115.
- [32] Z.-H. Xu, *The simulated distillation of heavy oil by supercritical extraction and fractionation*, M.S. Thesis, University of Petroleum, Beijing, 1994.
- [33] S. Zhao, Y. Zhou, Z. Xu, C. Xu, *J. Pet. Sci. Technol.* 24 (2006) 253.
- [34] G. Yang, R.-A. Wang, *J. Pet. Sci. Eng.* 22 (1999) 47.
- [35] C. Liu, C. Zhu, L. Jin, R. Shen, W. Liang, *Fuel Process. Technol.* 59 (1999) 51.
- [36] S. Zhao, Z. Xu, C. Xu, K.H. Chung, *J. Pet. Sci. Eng.* 41 (2004) 233.
- [37] C. Xu, J. Gao, S. Zhao, S. Lin, *Fuel* 84 (2005) 669.
- [38] S. Zhao, Z. Xu, C. Xu, K.H. Chung, R.-A. Wang, *Fuel* 84 (2005) 635.
- [39] H.J. Hoog, *J. Inst. Pet.* 36 (423) (1950) 738.
- [40] D. Yitzhaki, C. Aharoni, J. Am. Inst. Chem. Eng. 23 (1988) 342.
- [41] C. Philippopoulos, N. Papayannkos, *Ind. Eng. Res.* 27 (3) (1988) 415.
- [42] L.C. Trytten, M.R. Gray, E.C. Sanford, *Ind. Eng. Res.* 29 (5) (1990) 725.
- [43] C. Yang, F. Du, H. Zheng, K.H. Chung, *Fuel* 84 (2005) 675.
- [44] L.S. Kotlyar, B.D. Sparks, J.R. Woods, S. Raymond, Y. Le Page, W. Shelfantook, *Pet. Sci. Technol.* 16 (1998) 1.
- [45] L.S. Kotlyar, B.D. Sparks, J.R. Woods, K.H. Chung, *Energy Fuel* 13 (2) (1999) 346.
- [46] F. Bensebaa, L.S. Kotlyar, G. Pleizier, B.D. Sparks, Y. Deslandes, K.H. Chung, *Surf. Interface Anal.* 30 (2000) 207.
- [47] T. Jiang, R.A. Wang, G. Yang, *Proc. Int. Symp. Heavy Oil and Residue Upgrading and Utilization*, Fushun, PR China, (1992), p. 53.
- [48] S. Zhao, L.S. Kotlyar, J.R. Woods, B.D. Sparks, K.H. Chung, *Pet. Sci. Technol.* 18 (2000) 587.
- [49] D.L. Mitchell, J.G. Speight, *Fuel* 52 (1973) 149.
- [50] S. Zhao, B.D. Sparks, L.S. Kotlyar, K.H. Chung, *Pet. Sci. Technol.* 20 (2002) 1071.
- [51] S. Zhao, L.S. Kotlyar, J.R. Woods, B.D. Sparks, K.H. Chung, *Energy Fuels* 15 (1) (2001) 113.
- [52] R. Tanaka, J.E. Hunt, R.E. Winans, P. Thiyagarajan, *Energy Fuels* 17 (2003) 127.
- [53] S. Badre, C.C. Goncalves, K. Norinaga, G. Gustavson, O.C. Mullins, *Fuel* 85 (2006) 1.
- [54] Y. Zhao, M.R. Gray, *Energy Fuels* 15 (2001) 751.
- [55] J. Gao, L.S. Kotlyar, B.D. Sparks, K.H. Chung, *Pet. Sci. Technol.* 23 (3/4) (2004) 303.
- [56] E. Furimsky, R. Ranganathan, B.I. Parsons, *5th Canadian Symp. Catalysis*, Calgary, Alberta, October, 1977.
- [57] J.G. Speight, *The Chemistry and Technology of Petroleum*, Marcel Dekker, New York, 1999.
- [58] S.I. Andersen, J.G. Speight, *Pet. Sci. Technol.* 19 (2001) 1.
- [59] M.R. Gray, R. Zhao, G.M. McKnight, D.A. Komar, J.D. Carruthers, *Energy Fuels* 13 (1999) 1037.
- [60] S. Zhao, L.S. Kotlyar, B.D. Sparks, J.R. Woods, J. Gao, K.H. Chung, *Fuel* 80 (2001) 1907.
- [61] S. Zhao, L.S. Kotlyar, J.R. Woods, B.D. Sparks, J. Gao, J. Kung, K.H. Chung, *Fuel* 81 (2002) 737.
- [62] Y. Miki, S. Yamadaya, M. Oba, Y. Sugimoto, *J. Catal.* 83 (1983) 371.
- [63] M.R. Gray, F. Khorasheh, S.E. Wanke, U. Achia, A. Kryzwicki, E.C. Sanford, O.K.Y. Sy, M. Ternan, *Energy Fuels* 6 (1992) 478.
- [64] B.E. Stangeland, *Ind. Eng. Chem. Process. Res. Dev.* 13 (1974) 71.
- [65] Anonymous, *Oil Gas J.* 27 (December) (1993) 100.
- [66] K.P. De Jong, D. Reinalda, C.A. Emeis, in: B. Delmon, G.F. Froment (Eds.), *Studies in Surface Science and Catalysis*, vol. 88, Elsevier, Amsterdam, 1994, p. 155.
- [67] S.M. Richardson, H. Nagaishi, M.R. Gray, *Ind. Eng. Chem. Res.* 35 (1996) 3940.
- [68] M.R. Gray, Y. Zhao, C.M. McKnight, *Fuel* 79 (2000) 285.
- [69] M.A. Callejas, M.T. Martínez, T. Blasco, E. Sastre, *Appl. Catal. A: Gen.* 218 (2001) 181.
- [70] A. Hauser, A. Stanilaus, A. Marafi, A. Al-Adwani, *Fuel* 84 (2005) 259.
- [71] J.H. Gray, G.E. Handwerk, *Petroleum Refining Technology and Economics*, second ed., Marcel Dekker, New York, 1984 (Chapter 5).
- [72] S. Trasobares, M.A. Callejas, A.M. Benito, M.T. Martinez, D. Severin, L. Brouwer, *Ind. Eng. Chem. Res.* 37 (1998) 11.
- [73] S. Trasobares, M.A. Callejas, A.M. Benito, M.T. Martinez, D. Severin, L. Brouwer, *Ind. Eng. Chem. Res.* 38 (1999) 938.

- [74] K.H. Chung, J.K. Liu, Proc. Int. Conf. and Exhib. Petroleum Refining and Petrochemical Process, Beijing, China, 11–15 September, (1991), p. 234.
- [75] K.H. Chung, J.K. Liu, Proc. Int. Symp. Heavy Oil and Residue Upgrading and Utilization, Fushun City, China, 5–8 May, (1992), p. 125.
- [76] K.H. Chung, AOSTRA J. Res. 7 (1991) 259.
- [77] W.I. Beaton, R.J. Bertolacini, Catal. Rev. Sci. Eng. 33 (3/4) (1991) 281.
- [78] K.H. Chung, C. Xu, Fuel 80 (2001) 1165.
- [79] S. Zhao, L.S. Kotlyar, J.R. Woods, B.D. Sparks, K. Hardacre, K.H. Chung, Fuel 80 (2001) 1155.
- [80] Y. Tu, L.S. Kotlyar, B.D. Sparks, K.H. Chung, Pet. Sci. Technol. 24 (2006) 339.
- [81] S. Zhao, R. Wang, S. Lin, Pet. Sci. Technol. 24 (2006) 285.
- [82] S. Zhao, R. Wang, S. Lin, Pet. Sci. Technol. 24 (2006) 297.