Chapter 19

THE CHEMISTRY OF BITUMEN AND HEAVY OIL PROCESSING

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1. INTRODUCTION

Petroleum consists of a complex hydrocarbon mixture. The physical and chemical compositions of petroleum can change with location, age and depth. Beside carbon and hydrogen, the organic portion of petroleum contains compounds combined with sulphur, oxygen and nitrogen, as well as metals such as nickel, vanadium, iron, and copper.

In recent years, technological advancements in bitumen and heavy oil processing and the stabilization of crude oil prices have made production of synthetic crude oil from these resources attractive and economical. With the goal of processing heavy oil, bitumen, and residua to obtain gasoline and other liquid fuels, an in-depth knowledge of the constituents of these heavy feedstocks is an essential first step for any technological advancement.

It is well established that upgrading and refining of different feedstocks is related to their chemical properties. Since petroleum is composed of complex hydrocarbon mixtures, it is impossible to identify each individual component and its upgrading chemistry. Most investigations, to date, relate the thermal or catalytic behavior of petroleum feedstocks to their fractional composition. The hydrocarbon components of petroleum fall into three classes: [1]

1. *Paraffins* - saturated hydrocarbons, straight or branched chains but no ring structures;
2. *Naphthenes* - saturated hydrocarbons with one or more rings; these hydrocarbons may have one or more paraffinic side chains;

3. *Aromatics* - hydrocarbons with one or more aromatic nuclei; these hydrocarbons may be connected to naphthenic rings and/or paraffinic side chains.

In general, as the MW (molecular weight, or boiling point) of the petroleum fraction increases, there is a decrease in the amount of paraffins and an increase in the amount of naphthenes and aromatics.

This chapter briefly reviews the topics related to bitumen and heavy oil properties and their thermal chemistry; it includes:

- the chemical composition of heavy oil and bitumen in terms of fractional composition — an overview of the methods that have been applied to the separation of petroleum into hydrocarbon types;
- asphaltenes – physical and chemical properties, stability and thermal chemistry;
- chemistry of bitumen and heavy oil upgrading;
- reaction chemistry of bitumen components;
- application of hot stage microscopy;
- stability and compatibility of petroleum.

2. FRACTIONAL COMPOSITION OF BITUMEN/ HEAVY OIL

Conversion (upgrading) of bitumen and heavy oils to distillate products requires reduction of the MW and boiling point of the components of the feedstocks. The chemistry of this transformation to lighter products is extremely complex, partly because the petroleum feedstocks are complicated mixtures of hydrocarbons, consisting of 10^5 to 10^6 different molecules.[2] Any structural information regarding the chemical nature of these materials would help to understand the chemistry of the process and, hence, it would be possible to improve process yields and product quality. However, because of the complexity of the mixture, the characterization of entire petroleum feedstocks and products is difficult, if not impossible. One way to simplify this molecular variety is to separate the feedstocks and products into different fractions (classes of components) by distillation, solubility/insolubility, and adsorption/desorption techniques.[2] For bitumen and heavy oils, there are a number of methods that have been developed based on solubility and adsorption.[1] The most common standard method used in the petroleum industry for separation of heavy oils into compound classes is SARA (saturates, aromatics, resins, and asphaltenes) analysis.[3] Typical SARA analyses and properties for Athabasca and Cold Lake bitumens, achieved using a modified SARA method, are shown in Table 1. For comparison, SARA analysis of Athabasca bitumen by the standard ASTM method is also shown in this table. The discrepancy in the results between the standard and modified ASTM methods is a result of the aromatics being eluted with a mixture of 50/50vol% toluene/pentane in the modified method instead of 100 vol% pentane in the standard method. A different SARA composition was reported by Clark and Pruden when heptane was used to precipitate asphaltenes.[4] Compositional analyses, including SARA, for a number of Chinese and Middle Eastern vacuum resids were reported by Liu et al.[5] These authors also used modified SARA, which was developed in their laboratory (Table 2). In general, regardless of the method used, the properties of the feedstocks as determined by the SARA method give some indication of the "processability" or problems that may occur during upgrading of these relatively heavy materials. The knowledge of the chemical composition of the feedstocks, as will be shown later, plays a major role in predicting their behaviour in terms of phase separation, coke formation, molecular interactions, and the cause of catalyst deactivation.

Table 1. Properties and SARA fractionation results for Athabasca and Cold Lake bitumens

	Athabasca Modified ASTM 2007		**Athabasca ASTM2007**	**Cold Lake Modified ASTM 2007**		**Cold Lake ASTM 2007**
API Gravity			8.05		10.71	
	MW			**MW**		
Saturates (wt%)	381	17.27	16.9	378	20.74	21.52
Aromatics (wt%)	408	39.7	18.3	424	39.2	23.17
Resin (wt%)	947	25.75	44.8	825	24.81	39.36
Asphaltene (wt%)	2005	17.28	17.18	1599	15.25	15.95
Carbon (wt%)		83.34			83.62	
Hydrogen (wt%)		10.26			10.5	
Sulfur (wt%)		4.64			4.56	
Oxygen (wt%)		1.08			0.86	
Nitrogen (wt%)		0.53			0.45	
Residue (wt%)		0.15			0.01	

Table 2. SARA composition of various crudes[5]

Sample	Saturates wt%	Aromatics wt%	Resin wt%	C7 Asphaltene wt%
Daqing	34.8	35.5	29.5	0.0
Dagang VR	27.8	28.7	43.4	0.0
Guado VR	14.6	33.0	47.7	4.7
Shengli VR	16.1	30.6	51.1	2.2
Huabei VR	37.6	31.4	29.9	1.1
Liaohe VR	20.8	31.8	41.6	5.7
Oman VR	26.3	40.6	31.2	2.0
S-A-L VR	16.5	49.5	26.8	7.3

Since the trend with petroleum, including bitumens, is towards heavier feedstocks, greater emphasis will be placed here on the composition of material with high boiling point and molecular weight (MW). In a series of papers, Boduszynski[6,7] and Altgelt and Boduszynski[8,9] published data on the composition of heavy petroleum fractions up to the AEBP (atmospheric equivalent boiling point) of 760°C. The fractions were obtained by a combination of DISTACT distillation and sequential elution fractionation (SEF). Data from this work showed that heavy crude oils and petroleum residues had a wide range of MW distributions that extended to relatively small molecules. Quantitative analysis demonstrated that the MWs of most heavy petroleum components did not exceed 2000 g/mol. The hydrogen deficiency (aromaticity) of the petroleum fractions increased with increasing boiling point. The carbon content of petroleum feedstocks and their products varied over a narrow range (80-85wt%) whereas the difference between the hydrogen content of the feed and products varied over a much wider range (5-14wt%). Wiehe[10] suggested that the use of hydrogen concentration rather than H/C atomic ratio was more instructive for assessing fuel materials and processes. The work by Boduszynski[6,7] also showed that the distribution of sulphur, nitrogen and oxygen constituents of petroleum increased with increasing AEBP. It was further demonstrated that S and N associated with metals also occur in the same molecular structure.[6]

Recently, Chung et al.[11] applied SFE (Supercritical Fluid Extraction) to reveal properties of Athabasca bitumen resid. Using this technique, it was possible to fractionate Athabasca bitumen vacuum bottoms (VB) into narrow cut fractions (based on boiling point), the properties of which are shown in Table 3. Approximately 60 wt% of the residue was composed of relatively small molecules (500-1,500 g/mol). The remaining 40 wt% contained larger molecules, including asphaltenes, with an average MW of 1,500-4,200 g/mol. As the MW of the fractions increased, the fractions became more refractory (higher contents of S, N, metals and MCR (Micro Carbon Residue)). The fractions also became more deficient in hydrogen (lower H/C ratio). The use of this fractionation technique resulted in the removal of all asphaltenes and the concentration of the refractory material in the highest boiling point fraction. In comparison to oil sands bitumen, conventional crude oils are of better quality in terms of asphaltenes content. The crudes consist of small amounts of asphaltenes, a moderate amount of resins and a significant amount of oils.[12]

Table 3. Characteristics of Athabasca bitumen vacuum bottom fractions obtained by SFE technique[11]

	Fraction No.										
	1	**2A**	**2B**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**Pitch[b]**
Pressure MPa	4-5	5-5.5	5.5-6	6-7	7-8	8-9	9-10	10-11	11-12	>12	
Wt% of pitch	12.7	9.8	7.6	10.6	6.5	4.4	3.3	2.6	2.1	40.4	100
Density, g/mL at 20°C	0.975	0.993	1.006	1.023	1.043	1.054	1.065	1.068	1.074	N/A[c]	1.087
Molecular weight, Da	506	755	711	799	825	948	1134	1209	1517	4185	1191
Sulfur, wt%	4.0	4.5	5.0	5.4	6.0	6.2	6.5	6.8	6.8	7.6	6.5
Nitrogen, ppm	3080	4100	4330	5070	6160	6810	7370	7530	7900	10500	4600
Carbon, wt%	84.5	83.5	83.5	84	83	84	83	83	82.5	78.5	82.7
Hydrogen, wt%	11.5	11.15	10.95	10.55	10.25	10.05	9.8	9.7	9.5	8	9
C/H (atomci)	0.612	0.624	0.635	0.664	0.675	0.697	0.706	0.713	0.724	0.818	0.766
Aromatic carbon[a], fa	0.26	0.29	0.25	0.33	0.36	0.40	0.37	0.43	0.43	0.49	0.41
Nickel, ppm	12.8	21.3	30.1	44.8	71.1	89.7	123	138	162	339	148
MCR, wt%	5.6	7.9	10.8	14.3	18.2	21.5	24.7	26.5	28.7	78.9	26.7
Saturates, wt%	26.8	164	9.7	4.1	1.4	0.7	0.6	0.1	0	0	6.3
Aromatics, wt%	57.2	62.4	65.7	66.7	63.9	53.3	45.4	45.9	40.8	2	33
Resin, wt%	15.9	21.2	24.6	29.2	34.8	46	54	53.8	59.2	9.4	29.4
Asphaltenes, wt%	0	0	0	0	0	0	0	0	0	88.03	31.4

[a] C13-NMR. [b] Pitch = 524°C + fraction [c] N/A - not applicable

In recent years, the increased interest in refining of heavy crudes and processing VB from oil sands has clearly shown the need for a deeper knowledge of the composition and the chemical structure of these materials. At the National Centre for Upgrading Technology (NCUT) in Devon, Alberta, Canada, a series of fundamental studies was undertaken in order to understand the chemistry of bitumen and heavy oil VB and relate their chemical compositions to processing chemistry. The chemical properties of a number of heavy oils and bitumen VB are shown in Table 4. The data show that although the Forties VB contained a higher percent of pitch compared with the other resids, it also contained less asphaltenes, MCR, metal content, and heteroatoms. In order to gain more insight into the chemical properties of these vacuum residues, the maltenes (pentane solubles) of Athabasca, CL, and Forties VB were subjected to separation using a method similar to SARA analysis. VB maltenes were separated into saturates (M_1), mono/di-aromatics (M_2), polyaromatics (M_3) and polars (M_4). The data for Athabasca bitumen were first reported by Dawson et al.[13] and are compared with other feedstocks in Table 5**.**

Different laboratories may use different methods for the evaluation of feedstock quality. Method variation makes it difficult to compare the data among laboratories. For example, when comparing the properties of different feedstocks – for instance their SARA analysis – the feedstocks should have been distilled to the same nominal cut point. The data in Table 5 show that

Table 4. Properties of Feedstocks

Analyses	**Forties VB**	**CLVB**	**Lloyd VB/CLVB**
Density (15°C, g/mL)	1.039	1.039	1.03
Oils (wt%)	91.76	75.6	-
Asphaltenes (wt%)	8.15	24.4	20.9
Aromaticity, ^{13}C NMR	30	35	33 (31)
Pitch Content (+525°C, wt%)	93.7	75.4	74.1
MCR (wt%)	16.3	20.2	18 (18)
Molecular weight (g/mol)	948	1071	687 (800)
Viscosity (cST)			
100°C	509.1	2748	80.8 (at 60°C)
120°C	185.9	1010	-
135°C	100.8	377.8	-
Elemental (wt%)			
Carbon	87.1	82.66	84.44
Hydrogen	10.6	9.82	9.69
Nitrogen	0.43	0.51	0.58
Sulphur	1.24	5.42	5.43
Oxygen	<0.5	0.8	
Ash	-	0.04	0.1
H/C	1.46	1.42	1.37
Metals (ppmw)			
Vanadium	29	269	207
Nickel	13	104	96
Iron	3	175	-

Table 5. Components of vacuum resids (wt% on heavy oil/bitumen)

	Pitch (+525°C)	Maltenes (wt%)	Asphaltenes (wt%)	Saturates (M1)	Mono-diaromatics (M2)	Polyaromatics (M3)	Polars (M4)
Athabasca VB	96.4	59.9	40.1	3.36	3.18	38.1	15.36
Cold Lake VB	75.4	75.6	24.4	11.12	4.76	41.52	18.22
Forties VB	93.7	90.9	9.1	14.5	8.83	51.11	16.35

Athabasca bitumen VB and Forties VB have similar pitch contents (fractions boiling above 525°C) and that the concentrations of subcomponents of maltenes are also comparable. However, CLVB (Cold Lake vacuum bottoms) has much lower pitch content and the product composition cannot directly be compared with the other two feedstocks.

Another widely used technique for the separation of heavy oils into subcomponents is IEC (Ion Exchange Chromatography). In this method, the petroleum samples are separated into acid, base and neutral fractions. Walton[14] reported this technique in 1992, and it has also been used extensively by Green et al.[15] in studying the relationships between the composition of different feedstocks with product slate and composition in catalytic cracking. The properties of the Hamaca resid from Venezuela and its fractions, using the technique developed by Green, were reported by Rahimi et al.[16] and are shown in Table 6**.**

Table 6. Properties of Hamaca resid (+510°C) and its fractions

	Amphoteres	Bases	Acids	Aromatics	Saturates	Hamaca resid	Losses
Yield (wt%)	30	9.8	8.9	41.1	5.7		4.5
MW, VPO	1832	1048	996	600*	620*	NA[a]	
TGA 600°C Residue, wt%	43.4	19.2	24.9	5.5	0	NA[a]	
C	83	84.5	83.6	84.6	85.2	85.9	NA
H	8.2	9.6	10.4	11.5	15	9.7	NA
N	2.1	1.7	1.8	ND	ND	0.9	NA
O	2.9	1.6	2.5	1.6	<0.1	2.2	NA
S	2.8	2.8	2.3	2.5	<0.05	4.0	NA

[a] NA, not applicable. ND, not detectable. * values by desorption chemical ionization MS.

3. HETEROATOM-CONTAINING COMPOUNDS

Bitumens and heavy oils present a challenge for upgrading, partly because of their high levels of metals, N, S and O. There have been numerous publications related to organometallic compounds in heavy oils and bitumen, and the effects that they have during thermal and catalytic processing.[11,17-22] The concentrations of heteroatom-containing molecules such as sulphur, nitrogen and oxygen may be relatively small, but their influence during upgrading can be significant. Although heteroatoms are mostly concentrated in the heavier fractions, they are present throughout the range of boiling points. The presence of these molecules creates considerable process constraints during catalytic upgrading, causing catalyst poisoning and deactivation. In the finished products, these heteroatom-containing compounds also may cause problems, including lack of stability on storage and discolouration. Moreover, because of environmental issues future transportation fuels will contain no or significantly less heteroatoms compared with fuels today. Sulphur compounds in heavy oils, bitumen and transportation fuels have been studied by a number of investigators.[1,23-28] It has been shown in the asphaltenes fraction of petroleum that some of the sulphur in the sulphidic form connects two-ring structures (bridge) that can be easily cleaved under HDS conditions (300-345°C) and hydrogen pressures of 500-1,000psi.[1,29] Most S compounds are relatively easy to remove during hydrotreating. However, there are some that are very resistant and create problems during HDS reactions. There are excellent reviews by Whitehurst et al.[30], Toshiaki et al.[31] and Te et al.[32] regarding the HDS of polyaromatic S compounds. In general, it has been shown that the sulphur in ring compounds such as thiophene and benzothiophene can be removed rather easily during hydrotreating. Alkylation of the parent dibenzothiophene, especially at the 4 and 6 positions, reduces the catalyst activity for S removal because of steric hindrance.

Other molecules containing nitrogen and oxygen have a strong inhibition effect on desulphurization reactions.[33-35] H_2S, which is produced during HDS reactions, is also known to act as an inhibitor.

Because of the current limitations in HDS technology, Whitehurst et al, suggested alternative approaches listed below:[30]

1. Development of higher activity catalysts.
2. Altering the desulphurization reaction pathways for hindered sulphur compounds by using zeolite-containing catalysts.
3. HDS reactions that take place in more than one stage: modifying the feed in the first stage, such as isomerization of alkyl groups in hindered alkyldibenzothiophenes, to produce less sterically hindering positions for sulphur removal.
4. Developing a novel reactor design: knowledge of the composition and reactivity of sulphur compounds in different ranges has led to the design of a novel reactor. In this design, the desulphurization of lighter sulphur-containing compounds occurs in the top part of the reactor (co-current with the hydrogen stream). The higher boiling-point sulphur compounds react more efficiently, in the presence of catalyst, in a countercurrent mode.[36]
5. Developing a process other than hydrotreating: this involves the selective adsorption of sulphur compounds on materials such as activated carbon[37] and/or selective oxidation of the sulphur compounds followed by extraction[38-41].

There has been a significant increase in the number of studies to understand hydrotreating reactions for the development of HDN catalysts. Nitrogen compounds are known to be catalyst poisoning in hydrotreating processes[42] and are involved in the formation of gum, causing severe stability problems in the finished petroleum products[43].

Nitrogen content in petroleum and bitumen is much lower than sulphur content (0.1-0.9wt%), although some crude oils may contain up to 2wt%.[1] The amount of N increases as a function of boiling point, in a similar fashion to S. It has been shown that N concentration increases significantly around 350°C and continues to rise.[23] Nitrogen compounds can be classified into a) basic, including pyridine and its derivatives; b) neutral, including alkylindoles and alkylacridines; and c) acidic, including indoles, carbazoles, amides, and nonmetallic porphyrins.[1] Holmes,[44] demonstrated that most of the nitrogen in oil sands bitumen is tied up in pyridinic structures, including quinolines and acridines. Some molecules contain more than one N compound and others contain other elements such as oxygen and S in addition to nitrogen.[45] It should be pointed out that porphyrins are also considered nitrogen-containing molecules and their concentration is relatively high in the heavy distillates and asphaltenes fractions.

Although the chemical structures of some common N compounds are similar to their S counterparts, they behave differently under hydrotreating conditions. Based on the resonance energy of two-ring (Benzothiophene 56 kcal/mole vs. Indole 43 kcal/mole) structures there is no reason to believe that N removal would be more difficult than S removal.[42] However, from the available published data on N compounds, it can be concluded that the removal of nitrogen is indeed more difficult when compared with the removal of sulphur. Basic N compounds with a relatively low MW can be extracted with dilute mineral acids. Nitrogen compounds such as pyridine, quinoline, and isoquinoline also can be extracted from petroleum distillates using dilute mineral acids. However, the carbazole, indole, and pyrrole types of N compounds cannot be extracted with these acids.[1] In addition, N compounds can easily adsorb on the catalyst surface and inhibit other hydrotreating reactions. Removal of N requires prehydrogenation followed by hydrogenolysis of strong C-N bonds. In the transportation of fuels, traces of N compounds can have a significant effect on the stability of those fuels.

The oxygen content of petroleum is relatively small (<1wt%) and is concentrated in the heavier fractions (>350°C boiling point). The chemical functionalities of the oxygen-containing molecules include the following: hydroxyl groups (phenols), carboxyl groups (carboxylic acids and esters), carbonyl groups (ketones), and cyclic and acyclic ethers.[9] Phenols, carboxylic acids and naphthenic acids have been identified in a number of crude oils.[47] Ketones, esters, ethers, and anhydrides are difficult to identify because most of them occur in the higher molecular weight, nonvolatile residua.[1] Various analytical techniques, including LC and HPLC, have been developed to identify and quantify acidic compounds. Recently, using Ion Cyclotron Resonance Mass Spectrometry, Marshall et al. [48] identified over 3000 acids in heavy petroleum. However, in day-to-day refinery operation, a standard method (titration) is used for the measurement of the *total acid number*. In some crude oils, the concentration of acids reaches approximately 1 wt%. The presence of these acids is known to cause problems with corrosion in pipelines during transportation. It has been suggested that naphthenic acids react with iron salts to form iron naphthenates.[49] Upon decomposition of iron naphthenate, FeO is formed that reacts with S compounds such as H_2S, thiols, and disulphides to produce iron sulphide (Figure 1). Iron sulphide is involved in the fouling of refinery equipment. Formation of gum and sludge during storage of fuels can be attributed, in part, to the presence of phenolic compounds.[50]

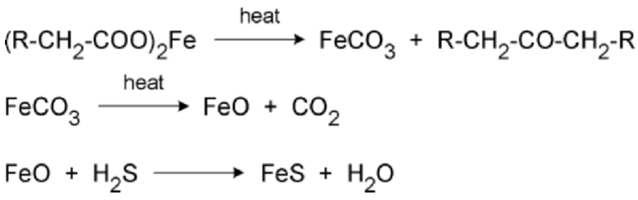


Figure 1. Mechanism of formation of FeS [49]

4. PROPERTIES OF ASPHALTENES (SOLUBILITY, MOLECULAR WEIGHT, AGGREGATION)

Petroleum consists of four hydrocarbon-types (saturates, aromatics, resins, and asphaltenes) that may be defined in terms of solubility, polarity, and MW.[1] Of these structural types, asphaltenes have markedly adverse effects on the processability of petroleum and play a significant role in the physical properties of heavy oils and bitumen. Because of these effects, in this chapter, asphaltenes will be discussed in detail in terms of their properties, composition, and thermal chemistry during upgrading, as well as their influence on instability/incompatibility during the production, transportation and upgrading of petroleum.

Asphaltenes are probably the most studied fraction of petroleum and bitumen. By definition, they are a solubility class: a fraction of petroleum that is not soluble in paraffinic solvents but soluble in aromatic solvents. In general, they are believed to contain large polynuclear aromatic ring systems ranging between 6 and 20 rings. The condensed aromatic structures bear alkyl side chains varying in size between 4 and 20 carbons.[51-53] Asphaltenes are also known to self-associate (aggregate) in solutions. The difficulty in measuring the MW of asphaltenes has been related to this phenomenon. Asphaltenes MWs as high as 300,000 g/mol (using the ultracentrifuge technique) have been reported.[53] Using the VPO technique, a MW of 80,000 g/mol for the same asphaltenes was reported.[53] Even lower MWs (1,000-5,000 g/mol) were reported in the same study for the same material using VPO under different conditions.

In terms of processability, aggregation of asphaltenes can hinder the conversion of heavy residues to lighter products and can enhance coke formation. Using surface tension measurements and rheological data, Sheu et al.[54-55] and Storm et al.[56] have shown that asphaltenes exhibit properties similar to colloids. These colloids exist in the heavy oil matrix in a micelle form.[57] Since the mole fraction of resins is higher than asphaltenes in petroleum, micelles are richer in resins. Asphaltenes also exhibit properties of colloidal systems such as the 'critical micelle concentration' (CMC) at which aggregates begin to form.

According to the asphaltenes-resin model, resins provide steric stabilization against precipitation of asphaltenes in petroleum fractions. The precipitation and phase separation of asphaltenes upon the addition of a nonpolar solvent can be rationalized in terms of a reduction in the solubility parameter or the polarity of the hydrocarbon medium.[58-60] The most direct evidence for the presence of asphaltenes aggregates in oil has been demonstrated by means of SANS (Small Angle Neutron Scattering). Ravey et al.[61] and Overfield et al.[62] further demonstrated that the physical dimensions and shape of the aggregates are a function of the solvent used. Ravey et al.[61] demonstrated that asphaltenes from Middle Eastern crude oils form sheet-like aggregates in tetrahydrofuran. Sheu et al.[54] showed that Ratawi asphaltenes in toluene and pyridine solutions form spherical aggregates having diameters between 60 and 66 Å. Watson and Barteau[62] observed STM (Scanning Tunneling Microscope) images of Ratawi asphaltenes aggregates separated from pyridine solutions, which showed that the asphaltenes aggregates formed orderly flat arrays covering hundreds of angstroms of the surface. The self-aggregation of asphaltenes plays an important role in the chemistry of asphaltenes conversion during thermal treatment of petroleum residues[63] and will be discussed in detail later in this chapter. Neves et al.[64] using light scattering and electrophoresis techniques, determined the aggregate size and charges present in asphaltenes from a Brazilian crude oil. When n-heptane was added to a mixture of asphaltenes in toluene, depending on concentration, the size of aggregate changed significantly varying between 125-186 nm in high concentration solutions to 238-398 nm in the low concentration solutions. It was also shown that asphaltenes possess a positive charge.

Asphaltenes from Athabasca bitumen were first separated using n-pentane by Pasternak and Clark in 1951.[65] In most refinery practices, the solvent of choice is n-heptane and asphaltenes are defined as materials soluble in toluene or a solvent having a solubility parameter in the 17.5-21.6 Mpa$^{1/2}$ range. As the carbon number of the extracting solvent increases, the amount of asphaltenes that precipitate decreases. Fundamentally, it is important to note that during asphaltene precipitation by any solvent, smaller asphaltene molecules, as well as some maltene materials, co-precipitate because of chemisorption. In order to obtain “pure asphaltenes,” Strausz et al.[66] suggested that after standard asphaltenes extraction, the material should be further extracted by acetone for one week. Following this procedure would result in asphaltenes that do not contain any foreign material. The formation of aggregates in Athabasca bitumen has been studied in detail by Murgich and Strausz.[67] It has been shown that the molecular shapes of asphaltenes and resins play a significant role in the sizes and lifetimes of the aggregates.

4.1 Chemical Structure of Asphaltenes

Recent studies by Strausz et al.[68-70], Strausz et al. and Peng et al.[71-72], and Murgich et al.[73] revealed the close structural similarities of asphaltenes from different sources. Asphaltenes are thought to be molecular units consisting of small- to mid-size alkyl and naphthenoaromatic hydrocarbons. Some units contain S and to a lesser extent N. The molecular units are linked together by C-C, C-S, and C-O linkages. A molecular representation of a petroleum asphaltenes model has been given by Artok et al.[74] This model was based on extensive analytical data using ^1H and ^{13}C NMR, GPC, pyrolysis gas chromatography/mass spectrometry, and MALDI TOF (Matrix-assisted laser desorption/ ionization time-of-flight) mass spectrometry.

Chemical and degradation methods were employed by Peng et al.[72] to study the structure of Athabasca asphaltenes. In the oxidation reaction of asphaltenes, the RICO (Ruthenium Ions Catalyzed Oxidation) reaction permits the selective oxidation of aromatics while leaving saturated hydrocarbons intact. A two-dimensional structure for Athabasca asphaltenes having the general formula of $C_{412}H_{509}S_{17}O_9N_7$, a H/C ratio of 1.23 and MW of 6,239 g/mol was proposed by Strausz et al. Recently, Leon et al.[75] investigated the structural characterization and self-association of asphaltenes having different origins. These authors argued that problems during crude oil production could be related to the asphaltene properties. They showed that n-heptane asphaltenes from two problematic crude oils had higher aromaticity, lower H/C atomic ratio, and significantly lower CMC (in different solvents) compared with the properties of asphaltenes derived from non-problematic crude oils. Although the data from this work could explain operational problems during crude oil production, the average structural model proposed for asphaltenes contains highly fused aromatics. This model is significantly different from the asphaltenes model proposed by Strausz et al.[66], which contains a smaller number of fused aromatic rings. In another study, Shirokoff et al.[76] investigated the structure of Saudi crude asphaltenes using compositional analysis as well as XRD (X-Ray Diffraction). Based on these analyses, it was concluded that the n-pentane asphaltenes derived in these crudes contained condensed aromatic sheets with a tendency to stack. The condensed aromatics had naphthenic and alkyl chains on their periphery. Yen et al.[77] postulated a similar structure with less dense alkyl regions on the periphery of asphaltene particles.

The effect of asphaltenes on the physical properties of heavy oils and bitumen has been studied extensively.[78-82] It has been demonstrated that the viscosity of petroleum is significantly influenced by the presence and concentration of asphaltenes. Storm et al.[81] demonstrated that when the relative viscosity of heavy oils was plotted versus asphaltenes concentration in both toluene (at room temperature) and vacuum residue (at 93°C), a straight line resulted. Thus, it was concluded that toluene is as good a solvent for asphaltenes as for vacuum resid. However, the amount of solvation is temperature dependent. By analyzing the temperature dependency of solvation, Storm et al. showed that the forces holding asphaltenes in the resid are very weak. Moreover, the fact that the solvation constant is the same for toluene at 25°C as in a vacuum resid at 93°C implies that the forces between asphaltene colloidal particles and toluene are weaker.

In a similar study aimed at shedding light on the aggregation of asphaltenes, Rao and Serrano[78] studied the physical interactions of asphaltenes in heavy oil. The viscosities of Arab resids containing different amounts of asphaltenes were measured in toluene at 27°C. It was concluded that aggregation of asphaltenes in heavy oils is stepwise and causes high viscosity and an apparent increase in MW. At low asphaltene concentrations, smaller aggregates were formed that could be dissociated to monomers at the processing temperature. However, at high asphaltene concentrations, the aggregates could not be dissociated and formed asphaltene clusters. Aggregate formation can cause process upset and limit process yields. Since formation of aggregates is stepwise and reversible, dissociation of asphaltene clusters to monomers may be accomplished by diluting the resid with an appropriate solvent, thus improving the process efficiency.

The dependency of feedstock viscosity on asphaltenes concentration has significant implications, because reducing viscosity could make pipeline transportation of heavy oil less dependent on diluent. Removal of even 100wt% asphaltenes from Athabasca bitumen does not reduce viscosity enough to meet pipeline specifications in Alberta (viscosity of 350 cSt at operating temperature, °API of 19, and BSW of <0.5 vol%). However, removal of approximately 30 wt% of asphaltenes has been shown to reduce diluent requirement by almost 30%. The benefit of partial removal of asphaltenes on thermal processing will be discussed later.

4.2 Thermal Chemistry of Asphaltenes

Asphaltenes are considered “bad actors” in refinery upgrading processes, because they cause coke and sludge formation, and in catalytic processes because they cause severe catalyst deactivation. It is widely accepted that petroleum is colloidal in nature and that asphaltenes exist in the petroleum in a micelle form. The formation of micelles is believed to be primarily due to the interaction between asphaltene species or asphaltene-resin fractions. The nature of the intermolecular or intramolecular forces that cause the formation of asphaltene micelles is not clear at present. It has been suggested that a number of forces may be involved including Van der Waals attraction, dipole-dipole interaction, hydrogen bonding, electron-transfer or charge transfer between aromatics (π-π bonding), and porphyrin interaction.[83-84] Wiehe [84] stated that the primary interaction between asphaltene molecules is the Van der Waals attraction between large areas of flat polynuclear aromatics. He used the solubility parameter to measure the attractive interaction between petroleum molecules, which is inversely related to the hydrogen content of the fractions. Using the generated phase diagram, it was shown that asphaltene molecules are relatively insoluble because of their high molecular weight and low H/C atomic ratio (high aromaticity). Wiehe also proposed a hybrid model for petroleum materials. According to this model, the asphaltenes are held in a delicate balance that can be easily upset by the addition of saturates or by the removal of resins and small aromatics.[85] During thermal treatment of petroleum feedstocks, the asphaltene micelles break down to form smaller aggregates. Further heating can result in the breakup of the protective resin layer and, finally, at about 300°C, the cores become “bare” resulting in precipitation of asphaltenes.

From a processing point of view, the microphase behaviour of asphaltenes plays an important role during catalytic and thermal upgrading of heavy oils and bitumens.[86-87] Storm et al. demonstrated that during hydroconversion of vacuum residues, the amount of sediment formation (cyclohexane insolubles) is strongly related to the amount of heptane insolubles in the residues.[86] When the heptane asphaltenes were removed from the residue, no sediment was formed. The authors further showed that a specific fraction of the residue, namely the pentane insoluble-heptane soluble fraction (which is relatively rich in hydrogen), plays an important role in reducing coke formation. They reasoned that the hydrogen in this fraction is used to cap the radicals generated in the asphaltenic-rich phase during conversion, hence retarding the formation of less soluble molecules.

Other properties of the feedstocks that could be correlated to the sediment formation are the degree of condensation of polynuclear aromatics and the degree of alkyl-substitution of polynuclear aromatics. In a later publication, Storm et al.[87] suggested the involvement of “macrochemistry” in the formation of sediment during hydroprocessing at lower temperatures. These particles (sediments) are then converted to macroscopic particles at higher temperatures. According to this model, grouping of certain molecules in the resid results in the formation of micelles with a dimension of 0.004:m. Rheological and SAXS (Small Angel X-ray Scattering) results showed that these small particles could be transformed into larger two-dimensional particles with dimensions of 0.02-0.03:m. As discussed earlier, these microstructure particles form well below temperatures that are characteristic of chemical reactions. Also, during low severity catalytic hydrocracking, polymerization between the larger two-dimensional particles does not occur and only a semisolid, which is soluble in the reaction media, is formed. However, at higher reaction temperatures, polymerization of the particles takes place and results in the formation of insoluble coke. It was thought that if the flocculation of larger particles could be interrupted below reaction temperatures, coke formation could be reduced. To reduce flocculation, Storm et al.[87] used 1 wt% of a polymeric additive (functionalized poly propyleneoxide diole with PCl_3) in a series of hydrocracking experiments with VB from Arabian medium and heavy crude oils. It was shown that the use of the additive, which was soluble in the heavy asphaltenic phase, interrupted the coalescence of asphaltic micelles required for coke formation. Thus, in these experiments, pitch conversion, desulphurization, and demetallation were improved and the formation of sediment was reduced.

In the pendant-core model proposed by Wiehe[88], every molecule in petroleum consists of two building blocks: an aromatic core, which is coke-producing, and a pendant block, which is attached to the core and can be cracked to produce volatile liquids. Using this model, the building blocks of each hydrocarbon type, including asphaltenes, were constructed. As the polarity or the boiling point of petroleum fractions increases, the core part of the fraction or its aromaticity also increases. As the resins and asphaltene fractions contain more cores, these fractions contribute significantly more coke than the other petroleum fractions during thermal processes. It has also been suggested that coke formation is the result of separation of a second liquid phase formed from partially converted asphaltene cores. The liquid-liquid phase separation is evidenced by the presence of spherical liquid crystalline coke called mesophase. The stacking of the polynuclear aromatic structure, present in asphaltenic material, forms the mesophase. During reside hydrocracking, mesophase lacks a significant degree of ordering (fast solidification) as a result of the high reactivity of the asphaltene cores. Wiehe[2] has shown in the thermal conversion of Cold Lake (CL) vacuum resid that there is a delay in coke formation (an induction period) and that the onset of coke formation is triggered by phase separation.

As indicated earlier, there is a delicate balance between the concentration of resins and asphaltenes in petroleum fractions. Any interruption in the ratio of asphaltenes:resins can cause operational problems because of asphaltene precipitation (coke formation) and plant shutdown. It is therefore crucial, if coke formation is to be minimized, to monitor the ratio of asphaltenes:resins during the thermal processing of bitumens and heavy oils. Clarke and Pruden[89] developed a heat transfer analysis technique that can detect the onset of asphaltene precipitation. They showed that precipitated asphaltenes could be re-peptized using polynuclear aromatic compounds such as phenanthrene. It has been demonstrated in the 5000 bbl/d CANMET hydrocracking unit operated by Petro-Canada at its Montreal refinery, that the recycling of heavy resids during the hydrocracking of heavy oils improves the plant's operability, resulting in higher conversions.[90] In Texas City, the H-Oil process for the catalytic conversion of resid blends has shown that the presence of highly aromatic byproduct streams is most effective in minimizing asphaltenes precipitation and solids formation.[91] The review by Mansoori[92] on asphaltenes deposition and control during production suggested that the addition of resins (peptizing agents) in proper amounts might prevent or control the heavy organic deposition problem.

Considering the "average chemical structure" of asphaltenes as proposed by Strausz et al.[66], understanding the chemistry of asphaltenes conversion could be extremely complicated. The literature suggests that asphaltenes, apart from producing coke, are also converted to lower molecular weight components that are later converted to liquid and gaseous products. Calemma et al.[93] studied the pyrolysis kinetics of four different asphaltenes using TGA/FTIR (Thermo Gravimetric Analyzer/Fourier Transform Infrared Spectroscopy). They concluded that for asphaltenes containing more sulphur, the activation energy was lower by about 2 Kcal/mole. The data were interpreted on the basis of weaker bond strength in C-S and S-S bonds, which are approximately 10 Kcal/mole lower than in C-C bonds. The data also showed that the activation energy increased at higher conversion. The results were explained as follows: as the reaction proceeds, the structures in the asphaltenes become more aromatic (dehydrogenation) and the alkyl groups attached to the rings become shorter. These reactions make the subsequent decomposition more difficult, which translates to higher activation energy for decomposition reactions.[94] Rahimi et al.[95] have shown that approximately 50 wt% of C_5 asphaltenes from Athabasca bitumen can be converted to maltenes at a relatively moderate severity.

During the thermal cracking of vacuum residues, maltenes play an important role in the conversion of asphaltenes. Wiehe[60] has shown that in the hydrocracking of CL VB (Cold Lake Vacuum Bottoms), the presence of maltenes in the resid increases (prolongs) the coke induction period significantly. The results were interpreted based on the effectiveness of maltenes as hydrogen donors to cap free radicals produced by the thermal cracking of asphaltenes.

At this stage, a general overview of the chemistry of upgrading is necessary prior to discussing the conversion of bitumen and heavy oil constituents at elevated temperatures.

5. CHEMISTRY OF UPGRADING

It is well documented that the conversion of resid to lighter products, whether or not in the presence of hydrogen and/or a catalyst, is largely thermally driven.[91,96] The hypothetical molecular structure of bitumen and asphaltenes consists mostly of C-C, C-H, C=C (in the aromatic rings) and to a lesser degree C-S, C-O, C-N, S-H, and O-H. The metal impurities are mostly attached to nitrogen in porphyrin and non-porphyrin structures. Since most of the chemical reactions during bitumen upgrading are thermally driven, there is no selectivity in bond cleavage. Under non-selective thermal reaction conditions, the weakest bonds break first. The bond dissociation energies of the most common bonds are shown in Table 7. According to this table, C-S (sulphide) has the lowest bond dissociation energy and will break first at a relatively moderate severity. At low to moderate severities in typical visbreaking conditions (380°C-410°C), 10-20wt% pitch conversion can be achieved without major coke formation. Under these conditions, the changes to the molecular structure of bitumen are relatively small since most of the C-C bonds remain intact. A significant MW reduction must take place before bitumen molecules are converted to distillates. The following chemical reactions are known to occur during this transformation to distillates:

1. homolytic cleavage of C-C bonds;
2. side chain fragmentation (cleavage);
3. ring growth;
4. hydrogen shuttling;
5. hydrogenation of aromatics/dehydrogenation of cycloparaffins;
6. ring opening;
7. heteroatom and metals removal.

Table 7. Bond dissociation energies

Bonds	**Kcal/mole**
H-H	103
C-C	83-85
C-H	96-99
N-H	93
S-H	82
O-H	110-111
C=C	146-151
C-N	69-75
C-S	66
Ar-CH_2-CH_2-Ar	71
Ar-H	111

The most important reaction in upgrading that leads to a significant molecular weight reduction and produces distillate fractions is probably cleavage of the C-C bonds. The bond dissociation energies for C-C bond cleavage can vary depending on the type of molecules. It has been suggested that the reaction mechanism for the cleavage of C-C bonds during upgrading is free radical in nature, and proceeds through a free radical chain mechanism.[97]

The reaction kinetic (homolysis) of a hypothetical molecule (M) proceeding through a free radical chain mechanism is shown in Figure 2. The overall reaction rate is related to the rate of the initiation step. If one assumes that the initiation step involves the homolytic cleavage of the C-C bond, then one can calculate the half-life (t ½) for the reaction. For example, the t ½ for the cleavage of the C-C bond in $PhCH_2$-$CH(CH_3)_2$ is 2.4 hours at 540°C and 46.3 days at 440°C. The fact that thermal hydrocracking of bitumens and heavy oils can be accomplished at a much lower temperature and a relatively high conversion indicates that the cleavage of C-C bonds is not a rate-determining step. The initiation step may involve cleavage of the C-S bond, or the breakage of the C-C bonds must be accomplished by a mechanism other than homolytic cleavage.

$$\begin{array}{ll}
\underline{\text{Initiation}} & M \xrightarrow{k_i} 2\,R^{\bullet} \\
\underline{\text{Propagation}} & R^{\bullet} + M \xrightarrow{k_p} RH + M^{\bullet} \\
 & M^{\bullet} \xrightarrow{k_{p2}} R'^{\bullet} + O \\
\underline{\text{Termination}} & R^{\bullet} + R^{\bullet} \xrightarrow{k_t} R\text{-}R \\
 & R^{\bullet} + M^{\bullet} \xrightarrow{k_t} R\text{-}M \\
 & M^{\bullet} + M^{\bullet} \xrightarrow{k_t} M\text{-}M
\end{array}$$

$$\text{Rate} = k_p\left(\frac{k_i}{2k_t}\right)^{1/2}[M]^{2/3}$$

Figure 2. Radical chain mechanism for homolysis of a hypothetical molecule M

There are a number of mechanisms proposed for the initiation step of the cleavage of strong C-C bonds. These reactions are shown in Figures 3 to 5. In the radical hydrogen transfer mechanism proposed by McMillen et al.[98], there is a direct transfer of hydrogen from a radical to another molecule. Another mode of transferring H atoms includes RRD (Reverse Radical Disproportionation), proposed by Stein et al.[99] Besides transferring an H atom from solvents, a free H atom can also be produced by β-elimination from various radicals or by the reaction of a stabilized radical with molecular hydrogen[100] (Figure 5).

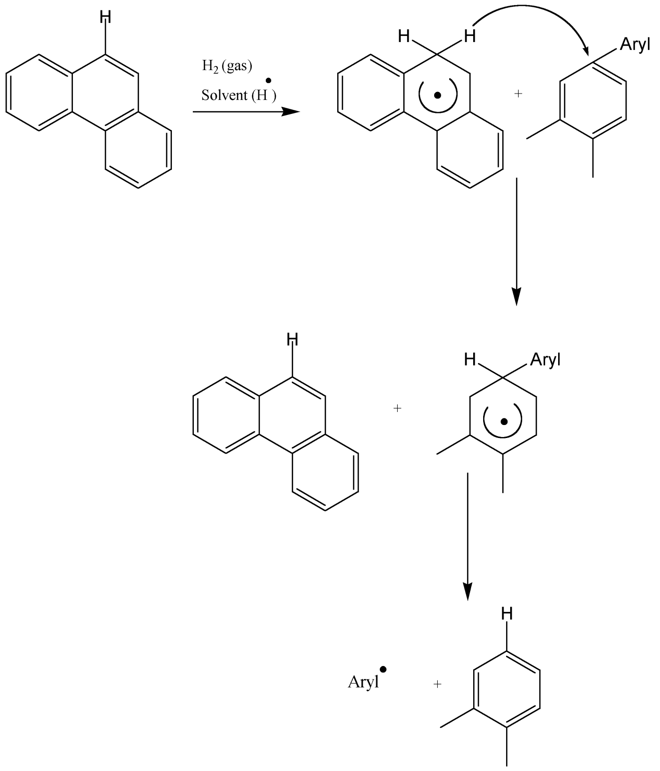


Figure 3. Radical hydrogen transfer for the cleavage of C-C bond[98]

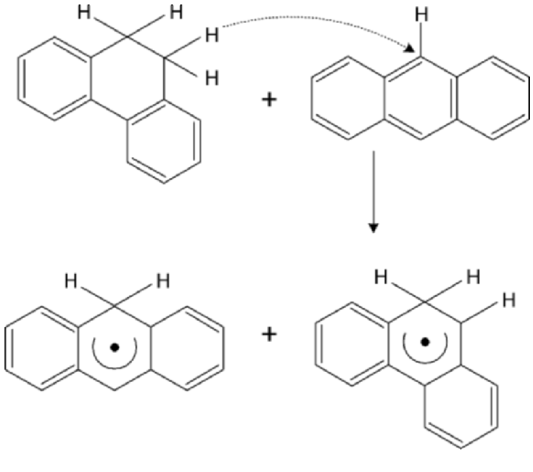


Figure 4. Reverse radical disproportionation mechanism for H-transfer [99]

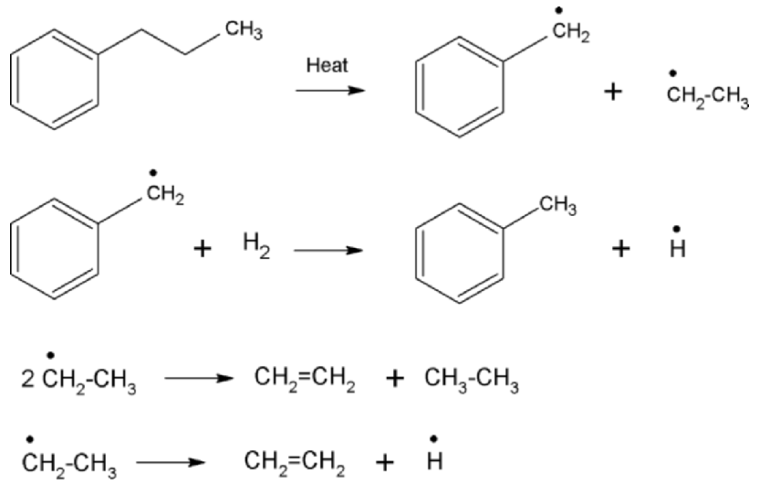
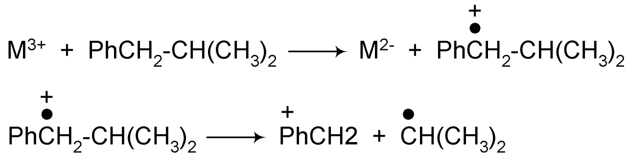


Figure 5. Formation of H by β elimination [100]

An alternative reaction mechanism to unfavorable homolytic C-C bond cleavage is the electron transfer mechanism shown in Figure 6. In this reaction, an electron is transferred from an aromatic core of a molecule to a metal (Ni, V, or Fe) to produce a radical cation. An electron transfer mechanism has been proposed for the reaction of the model in the presence of carbon black, and with tetralin as the solvent.[101] In this model, selective C-C bond cleavage (at the position of poly condensed aromatic moiety) is achieved at 320°C in the presence of carbon black where no thermal reaction is known to occur. The authors rationalized their observations based on the aforementioned electron transfer mechanism. The selective C-C bond cleavage occurs by an electron transfer from the condensed aromatic ring to the carbon black surface, which has become positively charged at a reaction temperature of 320°C. This reaction mechanism has been recently disputed by Penn et al.[102] They argue the C-C bond cleavage is caused by a radical hydrogen transfer mechanism in which the H atom adds to the ipso position of the polyaromatic moiety. It is also possible that this electron transfer may occur during bitumen and heavy oil upgrading since there is a significant concentration of transition metals capable of accepting electrons from highly condensed poly aromatics.



$$M^{3+} + PhCH_2\text{-}CH(CH_3)_2 \longrightarrow M^{2-} + Ph\overset{\overset{+}{\bullet}}{C}H_2\text{-}CH(CH_3)_2$$

$$Ph\overset{\overset{+}{\bullet}}{C}H_2\text{-}CH(CH_3)_2 \longrightarrow Ph\overset{+}{C}H2 + \overset{\bullet}{C}H(CH_3)_2$$

Figure 6. Cleavage of C-C bond via electron transfer mechanism

Whatever the reaction mechanism, it has been demonstrated in heavy oil upgrading that the conversion to lighter products is mainly thermally driven, whether or not the reaction is carried out in the presence of hydrogen and/or a metal catalyst.[103-106]

5.1 Reaction of Feedstock Components - Simplification of Upgrading Chemistry

The chemistry of resid upgrading is extremely complicated.[107-110] This is in part due to the complexity of the chemical nature of the feedstocks. In order to understand the chemistry of upgrading, it would be helpful to reduce this complexity prior to reaction, by separating the feedstocks (bitumen and heavy oils) into well-known components such as SARA – saturates, aromatics, resins and asphaltenes – which are useful tools in understanding bitumen chemistry.

Speight[111] investigated the chemistry of the thermal cracking of asphaltenes from Athabasca bitumen and deasphalted oil using a destructive distillation technique. A comparison of the analytical data from the feedstocks and products indicated that considerable changes occurred during cracking. The H/C atomic ratio data showed that simultaneous hydrogenation and dehydrogenation reactions took place. The results also indicated that DAO was more thermally labile than asphaltenes. Approximately 83 wt% of the DAO was converted into resins (maltenes), light oil and gases. In contrast, only 52 wt% of asphaltenes was converted into cracked products. The presence of n-paraffins in the light oil fractions indicated dealkylation (side chain fragmentation) of alkylaromatic compounds. A separate investigation of the thermal reaction of Athabasca bitumen at 440°C for 30 minutes using a micro-autoclave showed that approximately 46 wt% of pentane solubles (maltenes) was formed.[112] Further analysis revealed that the maltenes consisted of 17 wt% saturates, 5 wt% mono-/diaromatics, 20.5 wt% polyaromatics and 3.5 wt% polar compounds.

In a recent study by Rahimi et al.[113], partial deasphalting of Athabasca bitumen resulted in bitumen with an improved quality in terms of lower viscosity, MCR, and metals content. The better quality of the deasphalted oil was reflected in its coking behaviour. At laboratory conditions comparable to a delayed coking operation, deasphalted bitumen produced similar liquid yield but lower coke yield compared with the coking of the whole bitumen. Also, the liquid product resulting from the coking experiments of the partially deasphalted bitumen feed had less olefins. This product would be more stable and would need less hydrogen during upgrading and refining.

Klein et al.[114] investigated the pyrolysis kinetics of resids, isolated asphaltenes and maltenes from Hondo, Arabian heavy, Arabian light, and Maya oils. At 400°C and 425°C, isolated asphaltenes reacted selectively to form maltenes. At higher temperatures (450°C), asphaltenes reacted predominantly to form coke. Furthermore, pyrolysis of the maltenes indicated that asphaltenes and coke were formed in the following order:

maltenes → asphaltenes → coke

Karacan and Kok recently studied the pyrolysis of two crude oils and their SARA fractions.[115] Differential scanning calorimetry and thermogravimetry techniques were used to evaluate the pyrolysis behaviour of the feedstocks. The results indicated that the pyrolysis mechanisms depend on the nature of the constituents. Thermogravimetric data showed that asphaltenes are the main contributors to coke formation and that resins are a second contributor. The weight loss for the SARA components was additive. The authors argued that each fraction in a whole crude oil follows its own reaction pathway and there is no interaction or synergy between the components.

The chemistry of upgrading is expected to become significantly more complex when vacuum bottoms are processed. Dawson et al.[116] investigated the thermal behaviour of Athabasca bitumen VB and SARA fractions at temperatures between 420°C and 460°C. Detailed product analyses revealed that saturates and mono- and diaromatics are relatively unreactive, whereas polyaromatics and resins are converted to smaller molecules including saturates. The aromatic fraction constituted the major components of the vacuum residues. Approximately 54 wt% of CLVB consisted of polyaromatic hydrocarbons.[117] The upgrading chemistry of this fraction was investigated in a batch autoclave at different severity conditions (420°C-440°C, 30 min, 13.9 MPa H_2). The product analyses showed that at all severities the aromatic fraction (M_3) not only decomposed to form smaller molecules but also polymerized to form larger molecules and a small amount of coke (Table 8). The reaction sequence can be summarized as :

aromatics → resins → asphaltenes → coke

Table 8. Thermal hydrocracking of polyaromatics derived from Cold Lake vacuum bottoms

Products (wt%)	**420°C**	**440°C**	**450°C**
Gases	5.6	14.3	11
Asphaltene	6.0	9.5	12
Coke	0.7	0.5	0.3
Maltenes			
Saturates	10.3	15	21.7
Mono-diaromatics	8.4	9.8	9.1
Polyaromatics	57.8	33.1	41.6
Polars	11.2	17.7	4.6

Furthermore, the analysis of polyaromatic fractions following the reaction (M_3 products) showed that these molecules had relatively lower MW, shorter chains and were more aromatic. The results of this work confirm that side chain fragmentation and hydrogenation/dehydrogenation reactions are major routes in the thermal cracking of heavy oils and bitumen (see Tables 9-10).

Table 9. NMR analysis of M3 fractions from different sources

	Aliphatic carbon types (wt %)				
Source	Alpha CH_3	Naphthenic (Beta)	$>C_6$ Chains	Paraffinic CH	Others
Feed	8.5	4.9	6.1	9.4	24.2
420°C	6.8	2.8	4.4	9.3	18.1
440°C	6.6	1.7	1.1	5.1	13.9
440°C (cat)	7.6	3.1	4.3	8.5	19.6
450°C	7.1	1.5	0.9	5.2	14.3

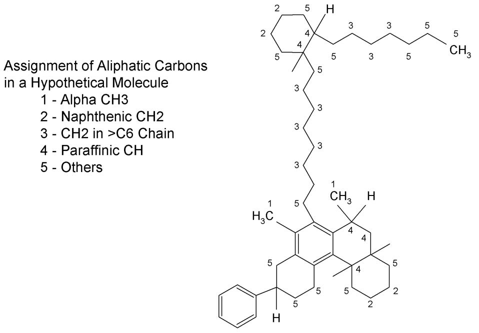
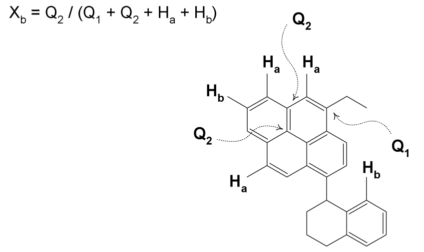


Table 10. NMR analysis of M3 fractions from different sources

	Aromatic carbon types (wt%)							
Source	Q1	Q2	Q1+Q2	Ha	Hb	Ha+Hb	Aromaticity	Cluster size*
Feed	9.0	8.5	17.5	5.8	6.3	12.1	0.36	14
420°C	11.1	10.1	21.2	11.1	8.7	19.8	0.50	12
440°C	11.4	20.2	31.6	15.7	8.1	23.8	0.66	18
440°C (cat)	10.4	10.7	21.1	10.8	9.4	20.3	0.49	12
450°C	14.3	13.1	27.4	17.2	9.3	26.5	0.65	11

χ_b = / (cluster size) given in reference (7)



In an attempt to correlate the thermal cracking behavior of heavy oils to their properties, Liu et al.[118] studied the thermal cracking of 40 heavy oil fractions obtained by supercritical extraction from six Chinese light crude oils and oils from Oman and Saudi Arabia. The thermal cracking experiments were performed at 410°C, 0.1 MPa N_2 for 1 hour. A non-linear regression fit indicated that the thermal cracking of the fractions could be correlated with the H/C, S (wt%), N (wt%) and molecular weight. A similar correlation was obtained with SARA analysis, S, and MW. In this study, the coke yields (toluene insolubles) correlated with the concentration of asphaltenes/resins plus aromatics of the cracked residues. These results were rationalized in terms of coke formation, not only from asphaltenes but also as a result of the phase separation of the colloidal system in the residues.

6. APPLICATION OF HOT STAGE MICROSCOPY IN THE INVESTIGATION OF THE THERMAL CHEMISTRY OF HEAVY OIL AND BITUMEN

Investigating the effects of process variables on coke formation is usually achieved by autoclave and pilot plant experiments, which are time consuming and expensive. Another tool that offers the advantage of real-time observation of the thermal reaction is hot-stage microscopy. This section reviews the usefulness of hot-stage microscopy for a better understanding of bitumen chemistry.[119]

The coke induction period (the time that is required for coke precursors or mesophase to start forming at a specific temperature) during thermal processing of heavy oils and bitumen is an important measurement for understanding operational problems. These problems may include coke formation and fouling in heat exchangers and fractionators leading to an unscheduled plant shutdown. The induction period coincides with the moment at which the asphaltenes in the reaction system reach their maximum concentration.[120] At the National Centre for Upgrading Technology's laboratory, hot-stage microscopy techniques were used to investigate those parameters that influence the thermal chemistry pathways during upgrading of petroleum feedstocks. Such studies could lead to possible solutions aimed at reducing coke and maximizing product yields. The parameters studied included the following: feed composition (i.e., SARA, acid, base); boiling point range (343ºC-675ºC); degree of asphaltenes removal (0-18 wt%, C_5 asphaltenes); coke suppressing agent (H-donors); and solid additives (clays) that inhibit coalescence of coke precursors.

6.1 Effect of Feedstock Composition

The thermal chemistry of heavy oils and bitumen is extremely complicated because of wide variations in chemical compositions. The most refractory components in petroleum feedstocks are asphaltenes, which contribute the most to coke formation during thermal cracking. Next to asphaltenes, resins and large aromatics also contribute to coke. To investigate the effect of these three heavy oil components on the mesophase induction period, Athabasca bitumen fractions containing varying amounts of asphaltenes (obtained by supercritical fluid extraction) and Venezuelan heavy oil fractions varying in polarity (obtained by Ion Exchange Chromatography) were selected.

One of the Athabasca bitumen fractions investigated under a hydrogen atmosphere consisted of 88 wt% asphaltenes. This fraction exhibited a very short induction period (48 minutes at room temperature), as expected for a highly-asphaltenic feed. These results are consistent with the findings of Wiehe[120], who demonstrated, using an autoclave, that Cold Lake asphaltenes (neat) formed coke immediately with no induction period. Using hot-stage microscopy it is also possible to follow the coalescence of mesophase particles in real-time and observe the changes in the apparent viscosity and, finally, the solidification process (Figure 7a). The second feedstock examined was a fraction of Athabasca bitumen containing 45.4 wt% resins, 54.0 wt% aromatics and no asphaltenes. The coke induction period was significantly longer (~72 minutes) compared with the fraction containing asphaltenes. This fraction developed mesophase of various sizes during thermal treatment, which later coalesced to form bulk mesophase and even-flow domains (Figure 7b).

In another study, in order to examine the relationship between reactivity and composition of a Venezuelan heavy oil, the Hamaca resid (510ºC+) was separated into fractions including amphoteric, acidic, basic, neutral and aromatic.[121] Results showed that the amphoteric fraction exhibited the shortest induction period for coke formation (50 minutes), followed by the basic and the acidic fractions. Amphoterics contain polynuclear aromatic systems having 5-6 rings per system [122]; as such, they are the most viscous and showed the fastest solidification. The basic fraction, which consists of 4 aromatic rings per system, showed a longer induction period (58 minutes). The acidic fraction, with only 1-3 aromatic rings per system, had an induction period of 68 minutes. The neutral fraction, which contains non-basic nitrogen and oxygen species, formed small mesophase spheres (Figure 7c) and the induction period was 82 minutes. The aromatic fraction had the longest induction period of 93 minutes and developed large mesophase (Figure 7d). The total resid containing all of the above components had an induction period of 61 minutes, indicating the synergy or interaction among the components during thermal reaction.

6.2 Effect of Boiling Point

Recently, major synthetic oil producers in Western Canada have switched from atmospheric bottoms to vacuum resids for processing bitumen. This raises the question of what impact this change might have on the coke induction period during thermal processing of these materials. To address this question, Athabasca bitumen (+343°C) was fractionated using Distact distillation into four distillates and resids.[123] The selected boiling point cuts were 525ºC, 575ºC, 625ºC, and 675ºC. The coke induction periods of bitumen and its resid fractions were measured under hydrogen and nitrogen atmospheres. The results indicated no major differences in the coke induction periods between bitumen (68 minutes) and the four fractions (68, 66, 77 and 61 minutes, respectively). This may have important process implications in that processing higher boiling fractions does not necessarily shorten the coke induction period.

Fig 7a: Semicoke formation from asphaltenes

Fig 7b: Semicoke formation from resins

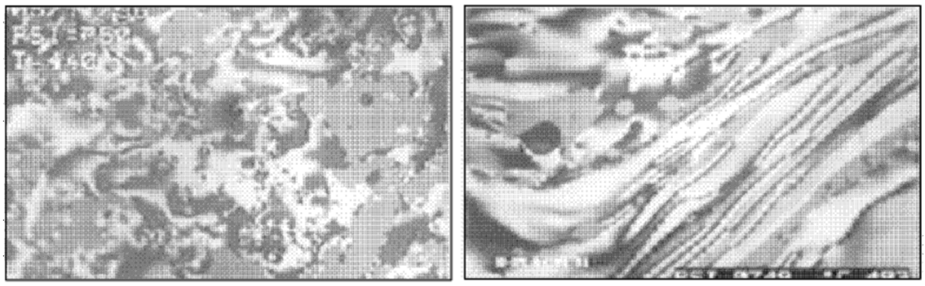


Fig 7c: Mesophase from neutral fraction

Fig 7d:Mesophase from aromatic fraction

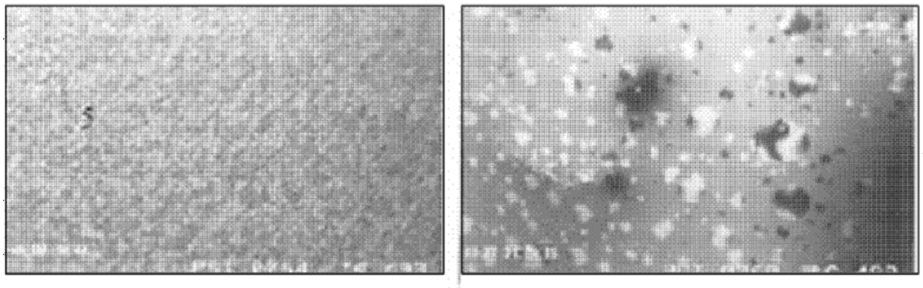


Fig 7e: Mesophase in presence of clay

Fig 7f: Mesophase in presence of H-donor

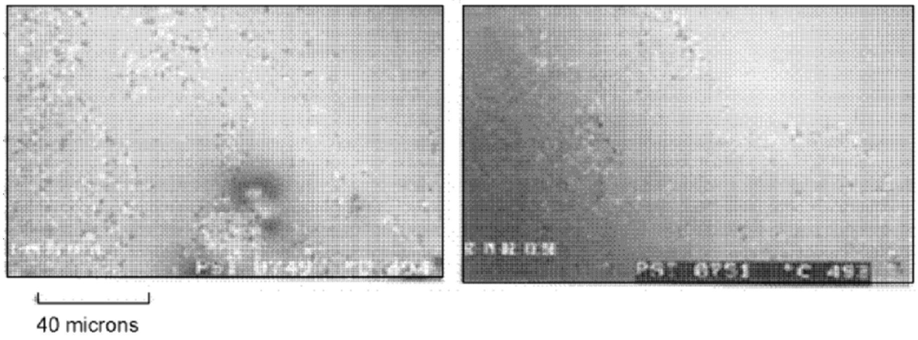


Figure 7. Effect of different variables on mesophase formation

6.3 Effect of Additives

Coke formation during thermal treatment of bitumen proceeds via the formation of mesophase spheres that coalesce to form larger mesophase, which eventually deposits as coke on the surfaces of equipment. If the coalescence process can be slowed down or prevented, the size of mesophase would be smaller and, consequently, be carried out of the process lines and vessels without fouling the equipment. To investigate the effectiveness of clay minerals as additives that interfere with the growth of mesophase, three clays (kaolinite, illite and montmorillonite) were added to Athabasca bitumen at concentrations of 2 wt% and 5 wt%.[124] Although the presence of clays did not result in a delay of the coke induction period, the presence of kaolinite reduced the size of mesophase and decreased the mesophase coalescence under nitrogen (Figure 7e). Thus, it was deduced that clays may reduce or prevent fouling on the walls of furnaces, exchangers and reaction vessels during bitumen upgrading.

Liquid additives, such as hydrogen donors, have also been shown to reduce coke formation during heavy oil hydroprocessing.[125] It has been shown that H-donors have the ability to scavenge free radicals, to act as antioxidants, and to inhibit coke formation while improving asphaltenes conversion. In order to examine the effectiveness of hydrogen donors on the induction period during upgrading, Athabasca bitumen vacuum bottoms was mixed with 5 wt% of an H-donor derived from a petroleum stream.[126] The results showed that the H-donor prolonged the coke induction period by as much as 20 min. It was also clear from the visual observation under microscope that the presence of additives reduced the rate of mesophase formation under nitrogen gas (Figure 7f).

6.4 Effect of Deasphalting

Asphaltenes are known to be the most refractory components in heavy oils and bitumen and can be converted to coke during thermal cracking. Therefore, it would be beneficial to selectively remove, if possible, the “worst” asphaltenes using solvents with different solubility parameters (polarity). To achieve the above objective, Athabasca bitumen was treated with mixtures of pentane and toluene ranging from P/T =100, 90/10, 85/15, 75/25 and 65/35. As the pentane to toluene (P/T) ratio decreased the amount of asphaltenes remaining in the partially deasphalted oil (PDAO) increased and their quality deteriorated, as indicated by progressively higher MCR content. To investigate the effect of asphaltenes removal on the coke induction period, the PDAOs were subjected to hot-stage microscopy studies.[127] It was shown that, as the P/T ratio decreased (solubility parameters increased), the coke induction period became shorter, ranging from 72 minutes at P/T=100 to 60 minutes at P/T=65/35. This study shows that deasphalting enhances the bitumen quality and results in a lower coking propensity.

7. STABILITY AND COMPATIBILITY

In nature, the components of petroleum, including bitumen and heavy oils, are in a fine balance. Any changes to this balance, as a result of physical or chemical treatments, can result in instability followed by asphaltenes precipitation, phase separation and sediment formation. In fact, the changes to the properties of petroleum occur from the time of its production and throughout transportation and processing. Asphaltenes precipitation can also occur when two petroleum streams are incompatible. Using the colloidal hybrid model for petroleum discussed earlier by Wiehe,[84] it is relatively easy to follow the changes in the structure of petroleum as a result of physical and chemical treatment. Either removing or converting the resins layer that protects (peptizes) asphaltenes, results in instability of asphaltenes and, finally, insolubility in the media and precipitation. To prevent further system deterioration, one must bring asphaltenes back into the solution (re-peptize), for example by the addition of small amounts of dispersants.

There are no standard tests for measuring the onset of asphaltenes precipitation. Among the techniques and analytical methods frequently used to measure sediment and asphaltenes onset for the adjustment of different process parameters in the refineries are:

1. spot test (ASTM-D-4740-95);
2. total sediment (ASTM-4870-96);
3. solubility parameters, optical microscope;[128]
4. light scattering (PORLA);[129]
5. peptization value (P-value);[130]
6. colloidal instability index (CII);[131-132]
7. coking index[133].

In recent years there has been a significant effort by different groups[129, 134-135] to automate the measurement of asphaltenes precipitation. This will, supposedly, create more reliable and consistent data.

In this section the stability and compatibility of petroleum will be discussed in terms of physical treatment such as distillation, deasphalting and diluent addition for pipeline transportation, and in terms of chemical treatment such as upgrading.

7.1 Physical Treatment

7.1.1 Effect of Distillation

Any physical treatment that may disturb the balance existing between components of oil may cause instability in the system and, finally, asphaltenes precipitation. One such physical treatment is distillation. Conversion of Athabasca bitumen to synthetic crude oil at both Syncrude Canada and Suncor Energy Inc., has changed from processing full-range bitumen (atmospheric bottoms, 343°C) to processing vacuum tower bottoms (524°C). Due to improvements in distillation technology, it is feasible to go to even deeper cut points without any cracking by using a short path distillation unit.

At the National Centre for Upgrading Technology in Canada, full-range Athabasca bitumen was distilled into four fractions using a DISTACT unit. The results on SARA analysis of the original feed and the fractions are shown in Table 11, and reveal that as the boiling point increased, the saturates, aromatics and resins decreased, whereas the asphaltenes content (C_5) increased significantly. As a result, the ratio of resins/asphaltenes decreased from 1.49 in the full-range bitumen to 0.30 in the fraction with a nominal boiling point of 675°C. As shown in Table 12, the stability as defined by the ratio of solubility number and peptization value (p-value) point to a less stable feedstock as the boiling point increases (although all fractions are stable and have values well above 1, which is considered to be the borderline between stable and unstable material). The fouling tendency as measured by the colloidal instability index (CII) showed that the feedstocks with a CII greater than about 0.6 would have a greater chance of forming deposits or coke when subjected to thermal treatment.[132] From the data in Table 12, it could be concluded that, although all the distillate fractions from Athabasca bitumen are stable, distillation into deeper cuts removed the asphaltenes' protective layers, making them more prone to separation/deposition and, subsequently, to coke formation.

Table 11. Effect of distillation cut point on SARA analysis of Athabasca bitumen

Cut point, °C	Saturates, wt%	Aromatics, wt%	Resins, wt%	Asphaltenes,wt%	Resins/asph
343	17.3	39.7	25.8	17.3	1.49
525*	5.9	31.8	20.8	41.5	0.50
575	5.3	30.9	19.7	44.1	0.45
625	4.8	23.3	17.1	54.7	0.31
675	3.5	20.4	17.5	58.5	0.30

* From DISTACT distillation

Table 12. Effect of cut point on satiability and solubility parameters of Athabasca bitumen

Cut point, °C	Resins/asph	S_{BN}/I_N	P-value	CII**
343	1.49	3.5	3.6	0.53
525*	0.50	3.0	3.1	0.90
575	0.45	2.4	2.7	0.98
625	0.31	2.5	2.4	1.5
675	0.30	2.4	2.5	1.6

* From DISTACT distillation

** Colloidal Instability Index = (S+Asph)/(A+P)

7.1.2 Effect of Addition of Diluent

Heavy oils and bitumen are very viscous (>100,000 cP) and as such cannot be transported by pipeline. The Canadian pipeline specification for viscosity is 350 cSt at operating temperature. At the present time, the viscosity specification is met by the addition of approximately 25 vol% diluent, usually natural gas condensate. Depending on the characteristics of the diluent, i.e., if it is paraffinic, it may cause asphaltenes precipitation during pipelining.

It is well known that the presence of asphaltenes in heavy oils and bitumen plays an important role in its rheological properties and is responsible for the observed high viscosity of these materials.[81] A recent study by Rahimi et al. showed that the viscosity of Athabasca bitumen varies significantly with the asphaltenes concentration.[127] Although the removal of all the asphaltenes from Athabasca bitumen (17wt% of C_5 asphaltenes) did not result in a product that met the pipeline specification for viscosity, the amount of diluent required to meet that specification was significantly reduced. It was further shown that a large excess of a paraffinic diluent (80 vol%) was required before asphaltenes precipitation occurred.[130] In the case of partial deasphalting for the purpose of producing cleaner feedstock, the largest and the most refractory asphaltenes could be removed by the addition of a small amount of paraffinic diluent. However, if the diluent in the bitumen is not removed immediately, the remaining asphaltenes might precipitate.

7.1.3 Thermal/Chemical Treatment

As discussed earlier, the asphaltene molecules are peptized by resins. In the deasphalting process, which is usually performed at low temperatures, the disruption between maltenes and asphaltenes is done deliberately and results in the precipitation of the latter. However, during thermal processes, the nature and the chemical characteristics of both maltenes and asphaltenes can change significantly. Because of the nature of the chemical reactions – such as side chain fragmentation – the paraffinic content of the reaction medium will increase. The reaction medium will not keep large molecules in solution and phase separation will occur. The reverse may also occur — wax (long paraffin chain molecules) separates because of a drop in temperature or an increase in the aromaticity of the liquid medium.[136]

There is another type of solid-like (coke-like) material formed during visbreaking and hydrocracking of vacuum residues. This type of solid is usually referred to as sediment or sludge. Sediment may form from both the inorganic or from the organic constituents of petroleum. Formation of sediment and sludge limits process conversion because of its accumulation in downstream equipment.[86] High severity (high conversion) processes promote condensation and polymerization reactions. When the solvent power of the liquid phase is not sufficient to keep the coke precursors in solution, coke is formed. Even during catalytic hydrocracking, such as in the H-Oil process, the formation of deposits cannot be avoided. The degree and the amount of deposit depend on the severity of the process. It has been shown that during H-Oil operation for moderate resid conversion (60%), there are no problems associated with sediment formation.[137] However, conversions above 60% are accompanied by increased fouling and sedimentation problems in the operating units. The fouling can be 1) the result of asphaltenes precipitation (phase separation) because of the incompatibility of the effluent stream; 2) the result of the formation of polyaromatics (PAH) from naphthenic hydrocarbons by dehydrogenation reactions; and 3) phase separation because of the existence of supercritical conditions in the hydroprocessing equipment.[138] However, the authors of this study believe that reactor fouling is mostly related to the rejection of Ni and V sulphides to the catalyst surface. Moreover, the extract from the deposit formed in the reactor was more aromatic than the feed to the H-Oil unit, indicating dehydrogenation under relatively severe conditions (440°C). From the analyses of the deposits obtained from the vacuum distillation tower, it was concluded that asphaltenes deposition is the major contributor to vacuum tower fouling in the H-Oil process.[137]

Incompatibility is believed to be the major cause of fouling during crude oil refining and hydrotreating when using a fixed-bed reactor.[138,139] Mixing crude oils may cause asphaltenes precipitation (incompatibility), which results in rapid fouling of the preheat exchanger and coking furnace tubes. Wiehe[138] has developed a compatibility model based on solubility parameters of crude oils. This model demonstrates that not only is the ratio of the blend important for obtaining a compatible mixture, but also the correct order of mixing crude oils will determine if the mixture is compatible. The incompatibility of oils has also been shown to result in the plugging of hydrotreaters. In Wiehe's study [139], the foulant accumulated in the top few inches of the bed and consisted of carbonaceous material with little inorganic matter (ash). In order to apply the oil compatibility model to oils that contain no asphaltenes, Wiehe developed new tests and was able to diagnose and resolve the plugging problem.

Polymerization and retrograde reactions lead to coke formation during thermal treatment of heavy oils and bitumen. Tests have been developed to diagnose the initial stage of the problem and prevent fouling. Depending on the thermal process used, there are different tests available to determine and control the sediment formed. The Shell hot filtration test is a common test used in hydrocracking to determine the stability of the operating process without possible shutdown. The amount of solids (n-heptane insoluble) formed is measured at intervals, and should not exceed a certain percentage (0.15-0.5 wt%) so that the stability of the operation can be maintained.

In visbreaking, which is a relatively mild thermal cracking process, the amount of asphaltenes in the visbroken residue (+350°C) increases and the ability of the medium to disperse asphaltenes decreases. The flocculation ratio of different concentrations of the resid is first determined using various concentrations of a binary solvent (n-heptane and xylene). A plot of the flocculation ratio versus the dilution ratio is then constructed. Extrapolation of the flocculation ratio to zero on the X-axis produces a value that is called the P-value (peptization value). This value must be higher than 1.1 (P-valve of the tar 350°C+ > 1.1). The stability of visbroken products from Athabasca bitumen obtained at different severities was reported recently by Rahimi et al.[130] During thermal reaction, the asphaltene aromatic cores, which were stabilized by aliphatic side chains and the presence of resins, were exposed by the cracking off of the side chains and by the conversion of resins. Thus, as the severity of the thermal process increased, the asphaltenes became increasingly less soluble (increased insolubility number). Thermal reactions also produce light hydrocarbons by breaking off the side chains from aromatic rings. This can result in a decrease in the solvency of the media (decreased solubility blending number). However, for the very aromatic Athabasca bitumen the solubility blending number remained nearly constant with increasing severity, showing that the light aromatic and light saturated products compensated for each other. Therefore, partially thermally cracked feedstocks are not only unstable because of the presence of olefins and diolefins, but also because the solubility of asphaltenes has significantly been reduced. The addition of hydroaromatic compounds (H-donors) significantly improves the quality and the stability of the visbroken tars.[140]

The stability of the reaction products in reactors can significantly be improved by controlling the resin:asphaltenes ratio. Benham and Pruden[90] demonstrated in the CANMET Hydrocracking Process® that controlling the ratio of polar aromatics to asphaltenes is the key to achieving a better unit operability and to obtaining higher pitch conversion and lower coke yield. By recycling the heavy gas oil fraction that is rich in polar aromatics, asphaltenes could be kept in peptized form leading to high pitch conversion with low coke yield.

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