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On-Column Separation of Wax and Asphaltenes in Petroleum Fluids[†]

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The utility of a novel method based on the new on-column precipitation and redissolution technique is explored. This method, called waxphaltene determinator (WAD), is strictly solubility-based and allows for the detection of waxes and asphaltenes in minutes. The principle of the method is to first precipitate waxes and asphaltenes together on a ground polytetrafluoroethylene (PTFE)-packed column using methyl ethyl ketone at −20 °C and then redissolve the precipitate with solvents of increasing polarity at different temperatures. Waxes precipitated under these conditions are composed mainly of *n*-alkanes, with carbon numbers greater than C_{20}, and heptane-soluble alkanes that are slightly to moderately branched. The method is first verified with model compounds, including *n*-alkanes and commercial waxes, and then applied to waxy crude oils and deposits. The method is compared to differential scanning calorimetry (DSC), and a linear correlation is found between the wax content by WAD and DSC. Asphaltene amounts by WAD also compare well to the gravimetric data.

1. Introduction

1.1. Background. Petroleum fluids produced from oil reservoirs are often transported and processed at pressures and temperatures where both waxes and asphaltenes may precipitate. These precipitates generate additional pressure drop in production tubings, pipelines, and surface facilities and eventually cause fouling.[1] Paraffins are composed of alkanes with formulas from $C_{18}H_{38}$ to $C_{70}H_{142}$.[2-5] These are straight- and branch-chained compounds that are generally inert and resistant to attack by acids, bases, and oxidizing agents. Early research postulated that *n*-paraffins are primarily responsible for this problem.[2] The determination of wax content in petroleum fluids can be used for a control of production and transportation processes as well as a guide to performance in many end uses. A number of procedures exist for the quantification of waxes and asphaltenes in petroleum fluids; however, they are often time-consuming and require large amounts of sample.

A new analytical approach to the characterization of polar materials in petroleum fluids, called asphaltene determinator (AD), has recently been developed.[6] This is a new technique of on-column precipitation and redissolution of asphaltenes. The development work and example separations with representative materials have been described in detail. The separations are performed using an inert stationary phase consisting of ground polytetrafluoroethylene (PTFE). Although high-performance liquid chromatography (HPLC) instrumentation and detectors are used, the separation does not involve chromatographic interactions between the material being separated and the stationary phase. It is strictly solubility-based.

In the current work, the utility of a novel method based on the new technique is explored. This method, the waxphaltene determinator (WAD), uses methyl ethyl ketone at −20 °C to precipitate waxes and asphaltenes together. The precipitated material is redissolved in four steps using solvents of increasing polarity at different temperatures: heptane at −20 °C, heptane at 60 °C, toluene, and then methylene chloride, both at ambient temperature (∼25 °C). This approach allows for the detection of waxy and polar materials in minutes. Methods based on the new technique are being evaluated with both up- and downstream petroleum fluids, such as crude oils, fuel oils, atmospheric residua, and vacuum residua. The current paper focuses on the utility of the method to evaluate waxes in crude oils and deposits.

1.2. Petroleum Waxes. Waxes in petroleum consist of branched and normal aliphatic molecules. They are typically classified into two major classes, paraffin and microcrystalline. Paraffin waxes are obtained from the light lube stock distillate of crude oil, and they typically have a melting range of 25−75

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(2) Nathan, C. C. Solubility studies on high molecular weight paraffin hydrocarbons obtained from petroleum rod waxes. *Trans. AIME* **1955**, *204*, 151−155.

(3) Hunt, E. B., Jr. Laboratory study of paraffin deposition. *J. Pet. Technol.* **1962**, *14* (11), 1259−1269.

(4) Burger, E. D.; Perkins, T. K.; Striegler, J. H. Study of wax deposition in trans Alaska pipeline. *J. Pet. Technol.* **1981**, *33*, 1075−1086.

(5) Newberry, M. E. Chemical effects on crude oil pipeline pressure problems. *J. Pet. Technol.* **1984**, *36*, 151−159.

(6) Schabron, J. F.; Rovani, J. F., Jr. On-column precipitation and redissolution of asphaltenes in petroleum residua. *Fuel* **2008**, *87*, 165−176.

°C.[1,7,8] Microcrystalline waxes are extracted from the residual lube stock of refined petroleum and have a melting range between 55 and 100 °C. Microcrystalline and paraffin waxes both consist of mixtures of straight- and branched-chain aliphatic hydrocarbon molecules. Petrolatum is a related material that consists of a complex mixture of hydrocarbons and various waxy materials that have a gelled appearance. Historically, it was obtained from deposits that were fouling equipment during oil production.

1.3. Wax Content. Classic approaches to the gravimetric determination of wax content are typically accomplished in a separation process consisting of a minimum of two steps. The initial separation consists of procedures such as deasphaltening, distillation, chromatographic separation on silica gel or alumina, urea adduction, or separation by preparative size-exclusion chromatography to isolate a fraction enriched in *n*-alkanes. The waxes separated in the first step can be analyzed directly by gas chromatography using a method such as ASTM D-5442,[9] differential scanning calorimetry (DSC) or separated further by freezing and precipitating the waxes in a polar solvent at sub-ambient temperature. Branthaver et al.[10] precipitated waxes by mixing a toluene solution of heptane maltenes from tar sand oil using methyl ethyl ketone (MEK, 2-butanone) at −20 °C. McKay et al.[11] isolated waxes from neutral fractions from ion-exchange chromatography separations of asphalts using a 2-butanone/toluene solvent mixture at −25 °C. Nwadinigwe and Eze[12] and Netzel and Rovani[13] used urea adduction followed by gas chromatography to characterize materials rich in *n*-alkanes. The European standard method for isolating waxes combines an initial distillation followed by precipitation of waxes from the distillate using diethyl ether/ethanol (1:1) (v/v) at −20 °C. Lu et al.[14] combined an initial separation using rod chromatography to isolate saturates, followed by separation of *n*-alkanes from this fraction by freezing and precipitation in MEK at −20 °C. They determined that *n*-alkanes with less than 20 carbon atoms do not precipitate in MEK at −20 °C, whereas larger *n*-alkanes freeze and precipitate. The upper limit of solubility in *n*-heptane at room temperature (∼25 °C) was determined to be about 40 carbon atoms (*n*-tetracontane). Lu and Redelius[15] compared two separations of waxes, by prepara-

Table 1. Selected Properties of Crude Oil Samples

sample	ρ^{20} (g/cm³) (DMA 4500, Anton Paar)	η^{20} (cP) (Cannon Fenske viscometer)	volatiles (wt %) (Rotavapor plus vacuum oven)	C_7−asphaltene (wt %) (ASTM D3279)
Minnelusa	0.9114	98.77	27.0	9.0
Tensleep	0.87143	25.75	31.8	3.2
LC	0.90435	58.59	29.7	4.0
Dakota	0.79869	7.09	63.5	1.2
Gullfaks	0.88376	20.74	40.2	1.0
Dagang	solid	solid	0.0	6.3

tive size-exclusion chromatography and precipitation of waxes from a distillate oil using diethyl ether/ethanol (1:1) (v/v) at −20 °C.

2. Experimental Section

2.1. Materials. Materials include heptane, toluene, chlorobenzene, methyl ethyl ketone (MEK), methylene chloride, octadecane (*n*-C_{18}), octacosane (*n*-C_{28}), and carbon disulfide, all 99% from Aldrich. Samples of paraffin and microcrystalline waxes consist of paraffin wax IGI 1245A (melting point of 60 °C), microcrystalline wax IGI 5788A (melting point of 60 °C), and microcrystalline wax IGI 5910A (melting point of 90 °C), all from the International Group, Inc. (IGI), commercial Gulfwax, and commercial Vaseline petrolatum. Crude oils consist of Minnelusa (Powder River Basin Field, WY), Tensleep (Oregon Basin Field, WY), LC (Alaska), Dakota (Fourteen Mile Field, WY), and Gullfaks (Norway). The crude oils are devolatilized by rotary evaporation at 70 °C for 2 h and placed in a vacuum oven overnight at 110 °C prior to analysis to eliminate losses of volatile components in the WAD detector. The properties of selected crude oils are provided in Table 1. We also used Dagang waxy crude oil (China), Boscan vacuum residuum (Venezuela), and wax deposits from sections 2 and 4 of Dakota reservoir (Fourteen Mile Field, WY).

2.2. WAD. *Procedure.* The new WAD separation uses MEK at −20 °C to precipitate waxes and asphaltenes together. The material soluble in MEK that elutes as a first peak consists mostly of aliphatic light oils, including *n*-alkanes with carbon atoms less than C_{20} and highly branched alkanes. Other functional groups, such as naphthenic or aromatic rings, may be present. The precipitated material is redissolved in four steps using solvents of increasing polarity and different temperatures: heptane at −20 °C (for low polarity oils and moderately branched alkanes, possibly containing naphthenic components), heptane at 60 °C (for *n*-alkanes with carbon

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(14) Lu, X.; Kalman, B.; Redelius, P. A new test for determination of wax content on crude oils, residues, and bitumens. *Fuel* **2008**, *87*, 1543–1551.

(15) Lu, X.; Redelius, P. Compositional and structural characterization of waxes isolated from bitumens. *Energy Fuels* **2006**, *20*, 653–660.
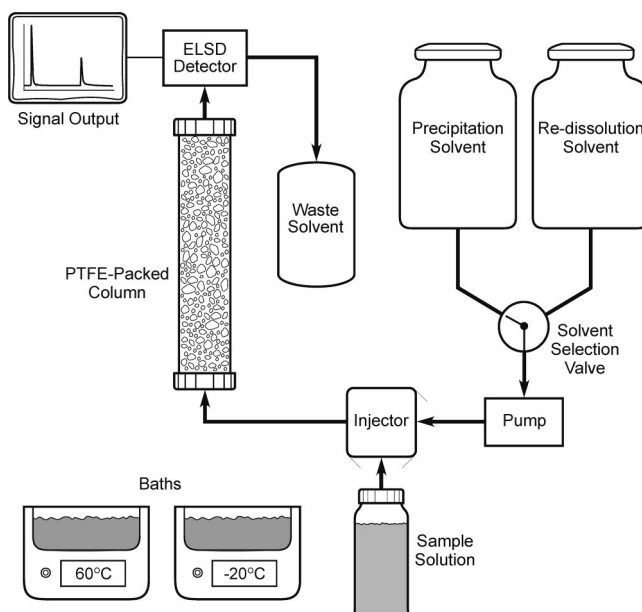
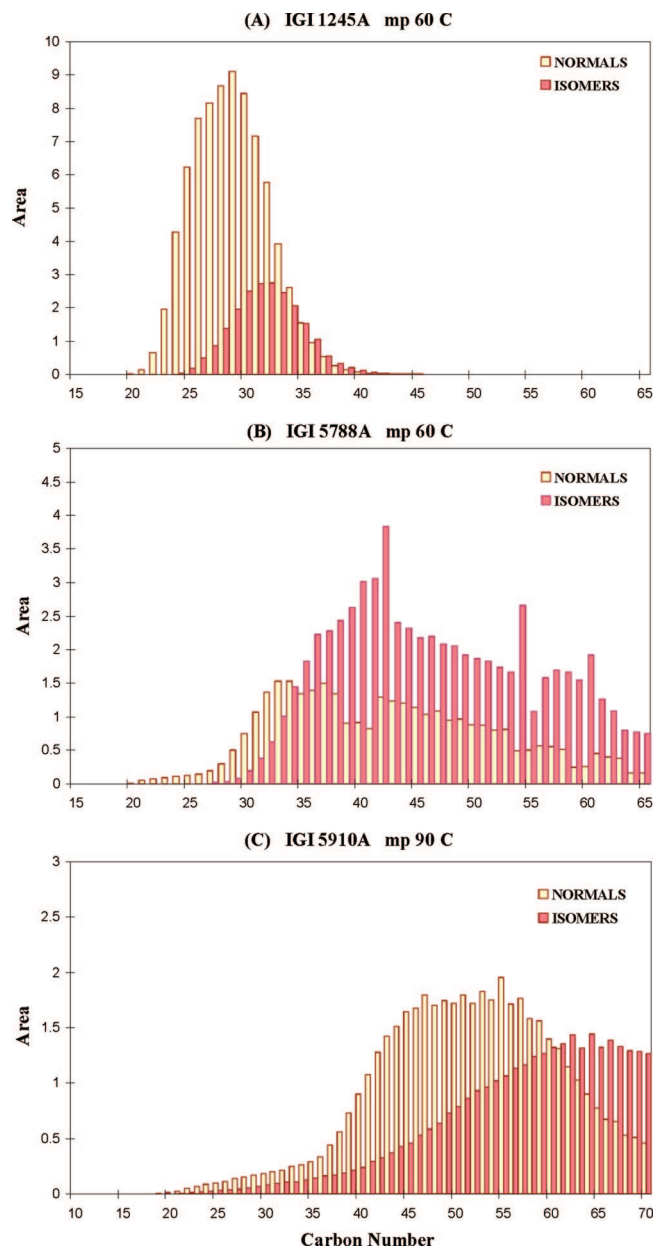

Figure 1. Schematic of the WAD.

Figure 2. High-temperature gas chromatograms of IGI paraffin and microcrystalline waxes.

atoms higher than C_{20} and slightly branched alkanes), toluene at ~25 °C (for asphaltenes), and then methylene chloride at ~25 °C (for higher polarity asphaltene components). A schematic of the instrumental configuration is provided in Figure 1. The development and demonstration of the on-column asphaltene precipitation and redissolution technique have been described in detail elsewhere.[6] The conditions used for the WAD separation are listed below:
- 250 × 10 mm stainless-steel column (Alltech 96511)
- 0.25−0.42 mm PTFE stationary phase (40−60 mesh)
- Solvent flow rate: 4 mL/min
- Step gradient times: The steps for the solvent and temperature step changes are shown in the figures. There is a slight lag of ~5 min between the time a step change is made before a peak appears at the detector. The step gradient times are 0 min,
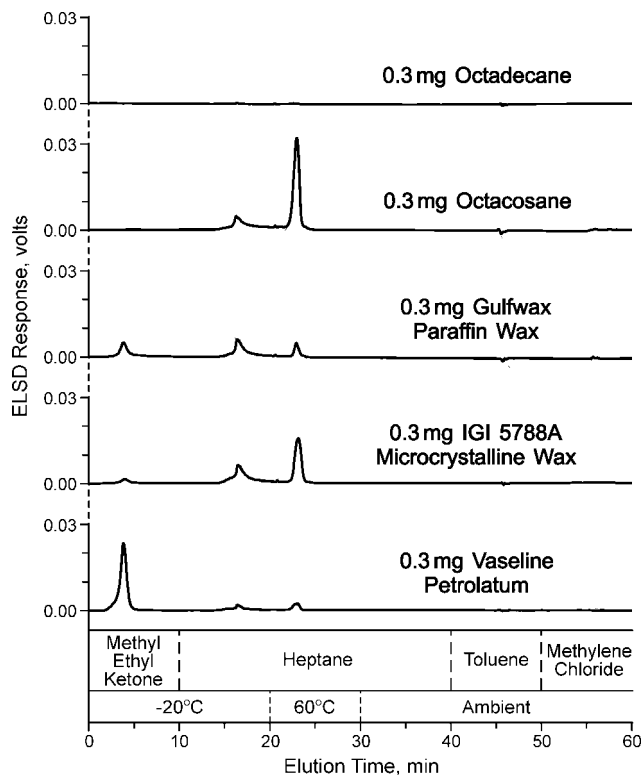

Figure 3. WAD separations of reference materials.

MEK at −20 °C; 10 min, heptane at −20 °C; 30 min, heptane at ambient; 20 min, heptane at +60 °C; 40 min, toluene at ambient; 50 min, methylene chloride at ambient
- Sample solutions: 10 wt % in chlorobenzene
- Amount injected: 10−20 μL (1−2 mg)
- Optical absorbance detector at 500 nm for standard quality check (QC) with Boscan residuum
- Evaporative light scattering detector: Waters 2424 ELSD, 12 °C nebulizer, 60 °C tube, and 50 psi nitrogen.

The optical absorbance detector cannot be used routinely with the WAD separation for waxy materials, because, once the waxy components are separated from the matrix oils, they tend to precipitate out in the optical cell, resulting in flow path plugging. Occasionally, cell fouling because of wax precipitation can occur in the evaporative light scattering detector (ELSD); however, this can be minimized by injections of very small sample portions.

2.3. DSC. *Procedure.* Wax determinations are performed using DSC in both cooling and heating cycles. A differential scanning calorimeter (Model Q2000, TA Instruments) is used for all analyses. In each test, about 10 mg of sample is sealed into an aluminum hermetic pan. An empty aluminum hermetic pan is used as a reference. The enthalpy of melting of indium and the indium melting point are used for the calibration of heat flow and temperature, respectively. The conditions for the cooling and heating cycles are as follows:
- Cooling
  - Equilibrate at 45 or 65 °C
  - Cool at 5 °C/min to −90 °C
- Heating
  - Equilibrate −90 °C
  - Modulate ± 5 °C every 80 s
  - Heat at 2 °C/min to 65 °C

Table 2. Aliphatic Hydrocarbon Distribution for IGI Wax Samples

	normal		branched		
sample	carbon number	maximum	carbon number	maximum	approximate branched/normal ratio
IGI 1245A paraffin	19−43	29	24−44	31	1:4
IGI 5788A microcrystalline	20−67	40	28−75	45	2:1
IGI 5910A microcrystalline	20−80	50	22−110	61	2:1

Table 3. WAD Area Percentages for Waxes

|		wax (area %)			
sample		moderately branched (heptane at −20 °C)	normal and slightly branched (heptane at 60 °C)	total	whole oil
octacosane		24.5	74.9	99.4	
IGI 5788A		40.7	51.9	92. 6	
Gulfwax		50.3	16.4	66.7	
Minnelusa	(test 1)	3.1	0.6	3.7	2.7
	(test 2)	2.9	0.5	3.4	2.5
Tensleep		5.3	0.2	5.5	3.8
LC		4.3	0.6	4.9	3.4
Dakota	(test 1)	9.1	7.5	16.7	6.1
	(test 2)	8.6	5.6	14.2	5.2
Gullfaks		2.4	0.3	2.7	1.6
Dagang		6.6	25.0	31.6	31.6
deposit 2		14.3	26.9	41.2	41.2
deposit 4		10.0	23.8	33.8	33.8

Analysis. The areas of the wax crystallization exotherms during cooling and melting endotherms during heating are used to estimate the wax content of the samples. This estimation requires a value for the heat of fusion of the wax as shown in the following equation:

$$\text{wax mass percent} = \frac{100(\text{endotherm or exotherm area in J/g})}{\text{wax heat of fusion}}$$

For these tests, the value used is 180 J/g. This value has been used in the wax measurement in petroleum samples with reasonable success.[16] In using this value, the assumption is made that the waxes present in the sample are predominantly macrocrystalline. The use of 180 J/g will result in underestimation of the wax content for microcrystalline waxes.

The thermal profiles during cooling and heating are sometimes complex and difficult to interpret or quantify. To aid the selection of end points, the derivative of cooling profiles is plotted. For heating profiles, the reverse heat flow (or heat-capacity-related signal) is used to help pick end points.
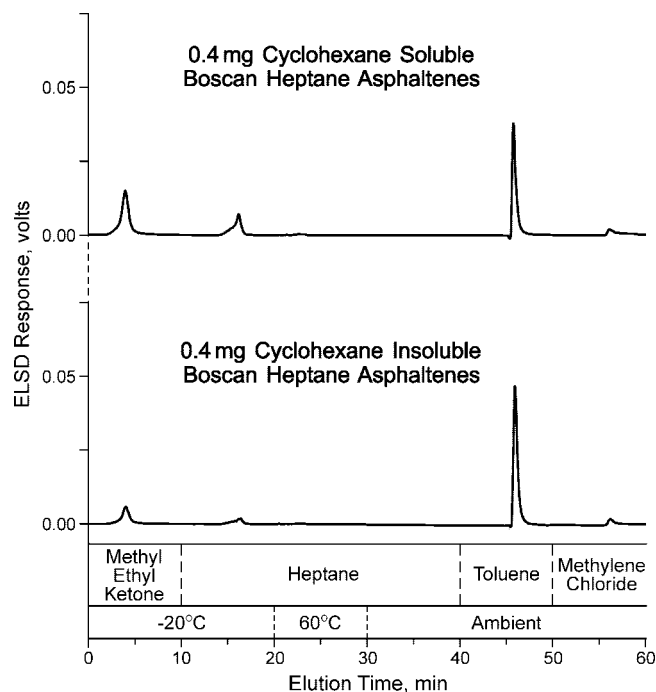
Figure 4. Separation profiles for cyclohexane-soluble and cyclohexane-insoluble asphaltenes.
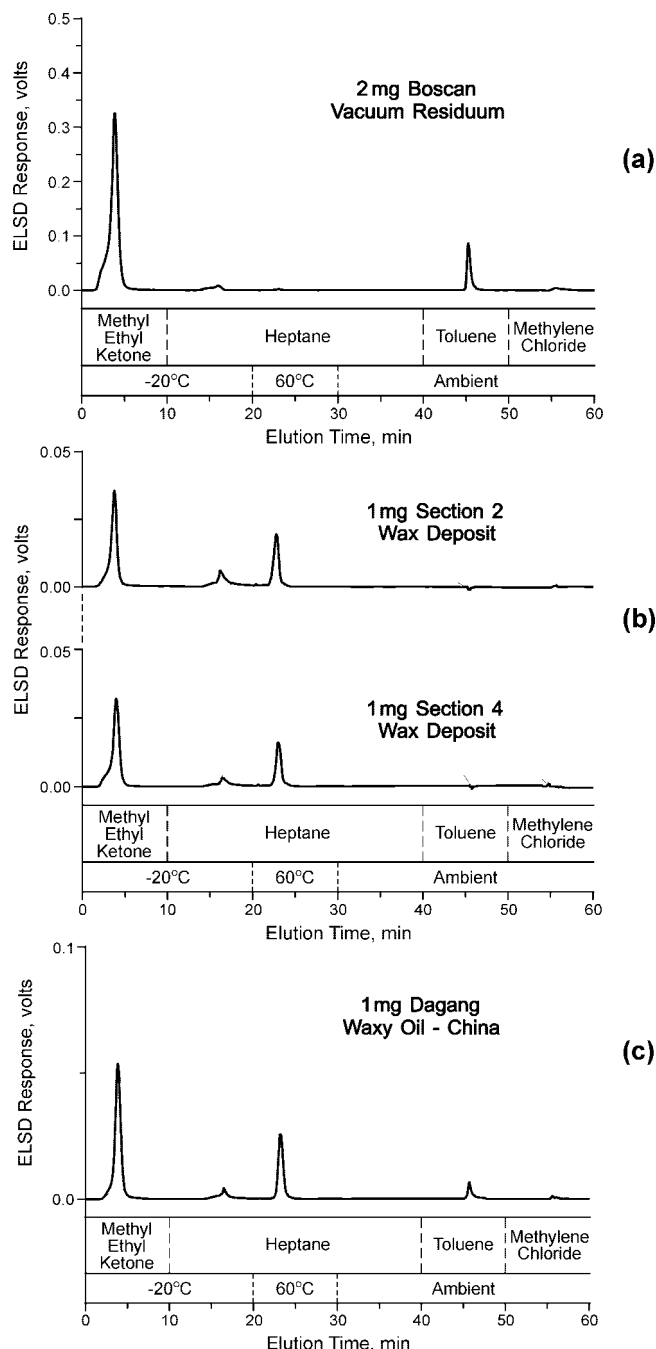
Figure 5. Separation profiles for (a) Boscan vacuum residuum, (b) Dakota wax deposits, and (c) Dagang crude oil.

2.4. High-Temperature Gas Chromatography (HTGC). *Procedure.* Gas chromatography (GC) is performed using a HP 5890 chromatograph with a flame ionization detector (FID) according to ASTM D6352. The operational conditions are given below:

- GC column Restek Poly wax 1000 lot A047169 (MXT-IHT) 5 m × 0.55 mm
- 2 µg/L injection of sample diluted in carbon disulfide
- Temperature profile rate
- Initial temperature: 40 °C
- 10 min at 40 °C
- Ramp 10 °C/min to 430 °C
- Hold 430 °C for 21 min
- GC conditions

(16) Michon, L. C.; Netzel, D. A.; Turner, T. F.; Martin, D.; Planche, J.-P. A ^{13}C NMR and DSC study of the amorphous and crystalline phases in asphalts. *Energy Fuels* **1999**, *13* (3), 602–610.

Table 4. WAD Area Percentages for Asphaltenes

		asphaltene polar component (area %)			
		polar (toluene at ~25 °C)	very polar (CH$_2$Cl$_2$ at ~25 °C)	total	whole oil
sample					
Minnelusa	(test 1)	4.7	2.5	7.2	5.3
	(test 2)	5.2	2.9	8.1	5.9
Tensleep		2.3	1.6	3.8	2.6
LC		2.0	3.0	5.0	3.5
Dakota	(test 1)	0.1	1.5	1.6	0.6
	(test 2)	0.4	2.4	2.8	1.0
Gullfaks		0.7	0.5	1.3	0.8
Dagang		5.0	0.0	5.0	5.0

- Injection temperature: 350 °C
- FID detector temperature: 430 °C
- Column head pressure: 120 kPa

3. Results and Discussion

3.1. WAD. *3.1.1. Model Compounds.* In the current study, several reference materials are evaluated to determine the elution characteristics of various chemical types in the new WAD separation. The selection of materials is based on their solubility in chlorobenzene at room temperature. The wax samples from IGI are first tested. GC profiles of branched (or isomers) and normal alkane distributions up to 70 carbons are provided by IGI and presented in Figure 2. All of the wax materials contained both branched and normal alkanes. By extrapolating the GC profiles, the range of branched and normal alkanes can be estimated. A summary of the *n*-alkane and branched alkane composition of these wax samples is provided in Table 2. Of all IGI waxes, only microcrystalline wax IGI 5788A is fully miscible at 3 wt % in chlorobenzene, probably because of the high ratio of branched to normal alkanes and relatively low melting point (see Figure 2). IGI 1245A forms dispersed flakes in chlorobenzene, and IGI 5910A forms a gel; hence, both waxes could not be evaluated by WAD. Instead, we used octadecane, octacosane, commercial Gulfwax paraffin, and Vaseline petrolatum. The separation profiles of the selected reference materials are presented in Figure 3. When 0.3 mg of octadecane is injected, peaks for heptane at −20 and 60 °C are barely visible because *n*-alkanes with less than 20 carbon atoms do not precipitate in MEK at −20 °C. However, there is no resolved peak for MEK. Instead, this material appears to gradually elute with MEK and heptane. By lowering the temperature further, i.e., −30 °C, and possibly using a solvent somewhat more polar than MEK, we may be able to resolve *n*-C$_{18}$ as a visible peak.

This problem is not encountered with Vaseline petrolatum, for which a clear peak of material eluted by MEK at −20 °C can be seen. With octacosane, the majority of the material (75%) elutes with heptane at 60 °C because octacosane has a carbon number greater than C$_{20}$, as shown in Figure 3 and Table 3. However, the small peak observed in Figure 3 suggests that a small portion of *n*-C$_{28}$ (25%) elutes with heptane at −20 °C. This may occur when the *n*-alkane carbon number is near C$_{20}$. Both Gulfwax paraffin and IGI 5788A microcrystalline wax contain a mixture of normal and branched alkanes. According to HTGC data in Figure 2 and Table 2, IGI 5788A wax contains about 64% branched alkanes and 33% *n*-alkanes, all with carbon atoms larger than C$_{20}$. Assuming that no *n*-alkane with carbon atoms larger than C$_{20}$ elutes with *n*-C$_7$ at −20 °C, the WAD area percentages in Table 3 together with HTGC data in Figure 2 indicate that IGI 5788A wax contains approximately 33% *n*-alkanes, 41% moderately branched alkanes, and 19% slightly branched alkanes.

3.1.2. Crude Oils and Deposits. Separation profiles for the cyclohexane-soluble and cyclohexane-insoluble/toluene-soluble portions of Boscan gravimetric heptane asphaltenes are provided in Figure 4. The results show that MEK at −20 °C elutes what can be described as base oils. Asphaltenes and waxy materials co-precipitate. Heptane at −20 °C likely dissolves relatively low polarity oil components, moderately branched alkanes, *n*-alkanes with carbon chains less than C$_{20}$, and other hydrocarbon material. The portion of polar asphaltene components that does not elute with MEK and heptane then elutes with toluene at ~25 °C, and the very polar asphaltene component materials elute with methylene chloride at ~25 °C.

A separation profile for Boscan residuum, which is used as a daily QC check material, is provided in Figure 5a. Separation profiles for two waxy deposits from Wyoming are provided in Figure 5b. The profiles for this material show significant normal and slightly branched alkane content. Indeed, when the column temperature is increased to 60 °C, the *n*-alkanes with carbon chains greater than the C$_{20}$ and slightly branched alkanes melt and dissolve in heptane and appear as a single peak. A separation profile for waxy Dagang crude oil from China is provided in Figure 5c. Significant normal and slightly branched alkane content is evident in this material, with the presence of some asphaltenes as well. Separation of waxes and asphaltenes was also performed on five devolatized crude oils. The area percents of the wax and polar asphaltene component peaks are provided in Tables 3 and 4. As can be seen, these crude oils exhibit relatively low wax and asphaltene contents. Material eluting

Table 5. Summary of DSC Results[a]

sample	treatment	onset (°C)		area (J/g)		mass (wt %)
		crystallization	melting	crystallization	melting	
Minnelusa	cooling	22.7		5.6		3.1
	heating		−34.2		8.3	4.6
Tensleep	cooling	19.7		20.9		11.6
	heating		−44.6		20.5	11.4
LC	cooling	33.5		14.6		8.1
	heating		−29.5		11.1	6.2
Dakota	cooling	33.9		94.5		52.5
	heating		−51.8		82.9	46.1
Gullfaks	cooling	19.1		6.0		3.3
	heating		−51.7		8.3	4.6
Dagang	cooling	37.8		129.7		72.1
	heating		−31.4		115.2	64.0
deposit 2	cooling	42.9		79.5		44.2
	heating		−61.0		80.8	44.9
deposit 4	cooling	47.7		74.3		41.3
	heating		−59.0		78.2	43.4

[a] The mass weight percent is calculated assuming a heat of fusion of 180 J/g.
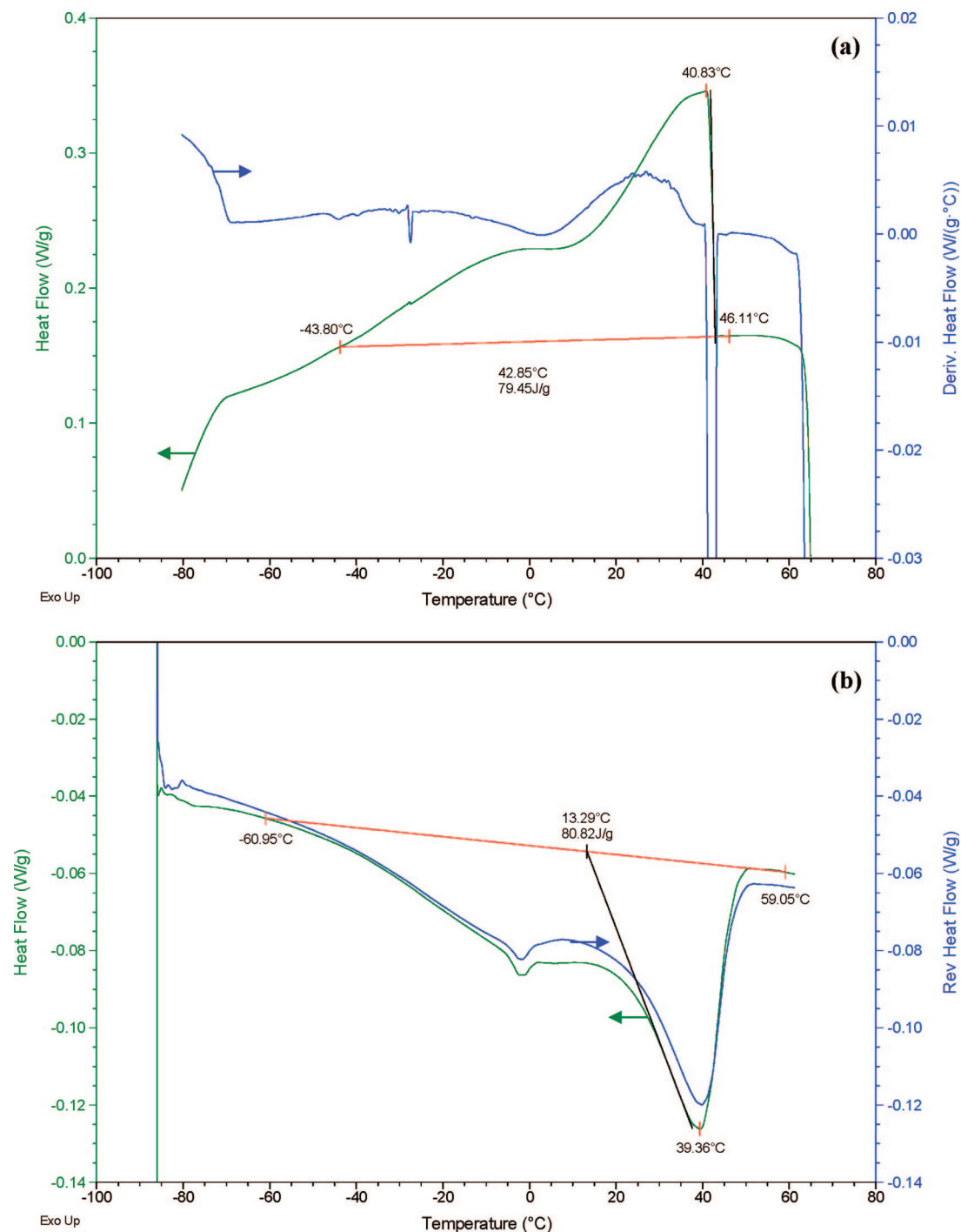
Figure 6. DSC of wax deposit section 2 under (a) cooling and (b) heating conditions.

near 16 min is classified as moderately branched, and material eluting near 22 min is classified as normal and/or slightly branched.

3.1.3. Solvency Considerations. For a material to dissolve in a solvent, the free energy, which consists of enthalpy, entropy, and temperature considerations, must be favorable (negative). For complex mixtures, such as petroleum, co-solvency and melting/freezing considerations for the various chemical components add to the complexity.

In petroleum systems, individual chemical components that are not soluble in a particular solvent can dissolve readily if they are part of a mixture with other species that impart co-solvency. For example, a significant portion of heptane asphaltenes from petroleum residua are not soluble in cyclohexane. However, the whole residua that contain these components

dissolve completely in cyclohexane.[17] Similar solubility behavior was observed with petroleum resins in *n*-alkanes.[18] In the AD separation, when a solution of gravimetric heptane asphaltenes is injected onto a PTFE-packed column with a heptane mobile phase, there is a component that remains soluble in heptane, while other components precipitate.[6] This is also confirmed with a preparative separation on a PTFE column followed by solubility evaluation of the heptane-soluble fraction in the current study. However, the whole asphaltene was originally isolated from the residuum by precipitation in heptane. The heptane-soluble materials are only soluble in heptane when they

(17) Schabron, J. F; Pauli, A. T.; Rovani, J. F., Jr. Molecular weight/polarity map for residua pyrolysis. *Fuel* **2001**, *80* (4), 529–537.
(18) Goual, L.; Firoozabadi, A. Effect of resins and DBSA on asphaltene precipitation from petroleum fluids. *AIChE J.* **2004**, *50* (2), 470–479.
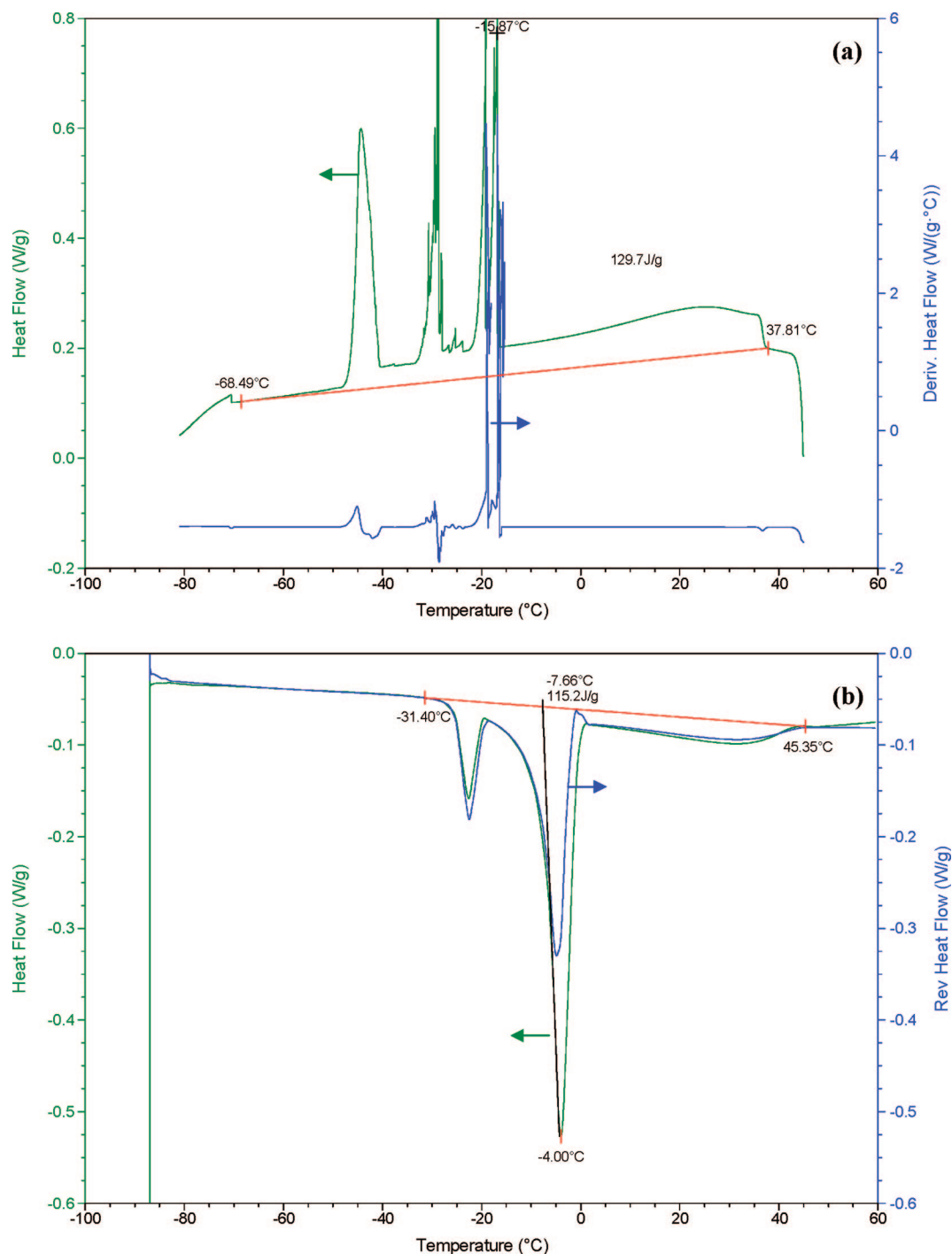
Figure 7. DSC of Dagang crude oil under (a) cooling and (b) heating conditions.

are separated from other components in the asphaltenes that render them insoluble. In addition, the PTFE column solubility separation indicates the presence of a highly conjugated component with extensive pericondensed ring structures that is poorly soluble in toluene and readily soluble in methylene chloride. However, the whole asphaltene is readily soluble in toluene when all of the components are together.

Co-solvency is also observed with wax components. For example, in the current study, we observed that octacosane (n-C_{28}) is only partially soluble in chlorobenzene at room temperature but dissolves completely when the mixture is slightly warmed under a lamp. However, microcrystalline wax IGI 5788A is fully soluble, and it contains n-alkanes from C_{20} to about C_{67}, including n-C_{28} (see Table 2). Co-solvency imparted

by the presence of branched hydrocarbons renders this material fully soluble in chlorobenzene at room temperature.

In addition to co-solvency, the melting and freezing of n-alkane components can occur also in a manner that affects solubility. An extreme example of alkane solubility is the dissolution of low- or medium-density polyethylene in decahydronaphthalene (decalin). The polyethylene material has a melting point of about 115 °C. This is the upper melting point range for n-alkane materials. Polyethylene will only dissolve in decalin when the temperature is near or above the melting point of polyethylene, once the polyethylene has melted.[19] The melted polyethylene is soluble, while the solid material is not.

Lu et al.[14] have observed that the temperature at which n-alkanes precipitate in MEK for separation from petroleum

Table 6. Comparison of Wax Content by DSC and WAD Methods

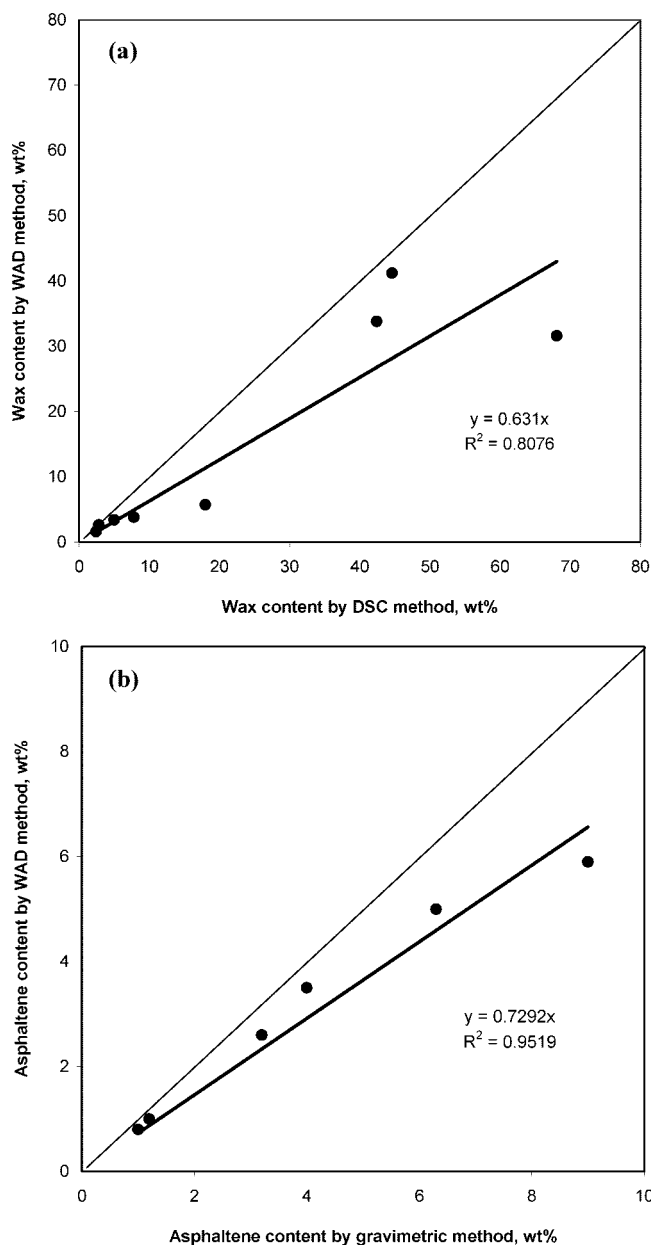|	DSC (wt %)		WAD (area %)			
sample	mean	whole oil	moderately branched	normal and slightly branched	total	whole oil
Minnelusa	3.9	2.8	3.0	0.6	3.5	2.6
Tensleep	11.5	7.8	5.3	0.2	5.5	3.8
LC	7.2	5.0	4.3	0.6	4.9	3.4
Dakota	49.3	18.0	8.9	6.6	15.4	5.7
Gullfaks	4.0	2.4	2.4	0.3	2.7	1.6
Dagang	68.1	68.1	6.6	25.0	31.6	31.6
deposit 2	44.6	44.6	14.3	26.9	41.2	41.2
deposit 4	42.4	42.4	10.0	23.8	33.8	33.8

materials is about 58 °C below the melting point of the *n*-alkane. With MEK at −20 °C, only *n*-alkanes with a carbon number of C_{20} or greater precipitate. At warmer temperatures, a combination of softening/melting and solubility in MEK results in the redissolution of the precipitated materials.

The combination of the co-solvency and freezing/melting effects in petroleum systems can be complex. These are also evident when individual chemicals or fractions are isolated from petroleum. These effects involve intermolecular interactions that can result in fouling during production, refining, and transport.

3.2. DSC. DSC tests are performed on devolatized crude oils and waxy deposits (see Table 5). The plots showing the area calculations for Dakota waxy deposit 2 and Dagang waxy crude oil are found in Figures 6 and 7, respectively. The profiles of crude oils are similar to the ones of waxy deposits. In most cases, it is difficult to find a clear low-temperature end point for the crystallization exotherms. A "best guess" based on the cooling profile and its derivative is used. The lack of a clear low-temperature end point also suggests that crystallization is incomplete. This is confirmed by the appearance of a "cold crystallization" exotherm during heating for some of the samples. In general, the heating profiles are easier to interpret, and endotherm areas obtained during heating should be more accurate. A summary of the results is in Table 5, and a discussion of the individual samples follows below.

Waxy Deposits. Waxy deposit section 2 has a sharp crystallization onset at 42.9 °C during cooling (Figure 6a), and the exotherm extends to about −44 °C. The low-temperature end point is estimated from the derivative curve and extrapolation. The heating profile (Figure 6b) shows an endotherm beginning about −61 °C and extending to about 50 °C. The low-temperature onset of this endotherm is estimated using extrapolation. The onset for crystallization during cooling for wax deposit section 4 is 47.7 °C. The low-temperature end point, −48.0 °C, is estimated from the derivative curve and extrapolation. Extrapolation is also used to estimate the melting endotherm onset for the heating cycle.

Dagang Crude. The cooling profile for this sample (Figure 7a) shows a broad crystallization exotherm and four very sharp, very energetic exotherms. Approximately half of the total area of the combined exotherms is contained in these four events. The other half of the area is contributed by the broad exotherm, which has an onset of 37.8 °C and appears to extent to at least −50 °C. The heating profile (Figure 7b) is simpler, with a broad endotherm and two sharper endotherms. In this profile, the two sharp endotherms contribute 67% of the area, with the balance being the area of the broad endotherm.

(19) Schabron, J. F; Fenska, L. E. Determination of the antioxidant additives BHT, Irganox 1076, and Irganox 1010 in polyethylene by high-performance liquid chromatography. *Anal. Chem.* **1980**, *52*, 1411.
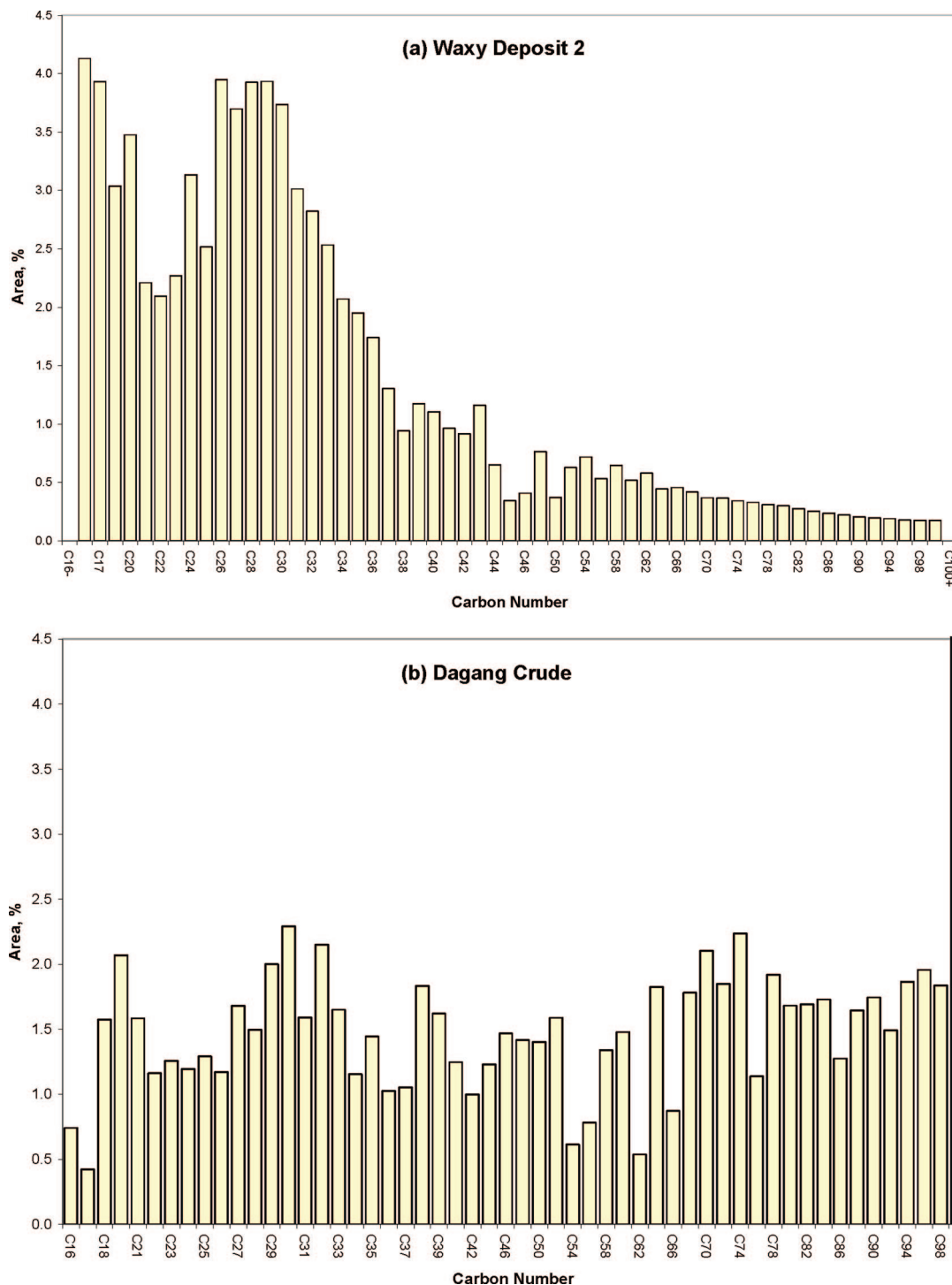

Figure 8. Comparison of (a) wax and (b) asphaltene contents by WAD and other methods.

Minnelusa Crude. The cooling profile indicates a crystallization onset at 22.7 °C, with a maximum rate at 2 °C. We estimate a low-temperature end point about −31 °C. The heating profile shows a well-defined melting endotherm from −39 to 40 °C. The peak at −60 °C is due to the crystallization of waxes that nucleated during cooling but had insufficient time or mobility to crystallize. Typically, the onset temperature of this "cold crystallization" exotherm occurs close to the midpoint of the glass transition.

Tensleep Crude. The cooling profile shows a crystallization onset at 19.7 °C. This sharp onset is characteristic of a material that undergoes supercooling, then nucleates, and crystallizes rapidly. The low-temperature end point is estimated to be about −51 °C. The heating profile shows a well-defined large melting endotherm from −53 to 35 °C. There is a small cold crystallization peak centered about −65 °C.

LC Crude. The cooling profile has an apparent crystallization onset at 33.5 °C, but the end point is very difficult to find. We estimate a value of −39.7 °C based on the shape of the derivative curve. During heating, however, there is a clear

Figure 9. HTGC distribution of normal alkanes in (a) wax deposit 2 and (b) Dagang crude.

melting endotherm from −29 to 57 °C, a cold crystallization exotherm centered at −48 °C, and a glass transition centered about −65 °C.

Dakota Crude. The cooling profile shows a very large crystallization exotherm with a sharp onset at 33.9 °C. The end point is estimated from the derivative curve to be about −49 °C. The heating profile has one large endotherm from −51.8 to about 40 °C. The low-temperature melting onset is estimated by extrapolation from the high-temperature baseline.

Gullfaks Crude. This sample shows clear onset and end points upon cooling. Crystallization starts at 19.1 °C and ends at about −52 °C. In the heating profile, there is a clear glass transition centered about −70 °C, a cold crystallization

exotherm centered about −60 °C, and a melting endotherm stretching from −51.7 to 36.0 °C. The low-temperature onset for this melt is selected on the basis of the shape of the reversing heat flow profile.

The wax contents shown in Table 5 are based on an estimated heat of fusion of 180 J/g, which correspond mainly to macro-crystalline wax. For some samples, the broad melting and crystallization region may indicate a substantial amount of branched alkanes that are not detected by DSC. The Dagang oil sample is much different than the other samples and contains some components that energetically crystallize after supercool-ing. These could be pure alkane compounds or other crystallizing material. Other than obtaining crystallization onset temperatures,

the data obtained from the cooling experiments are not as reliable as the data from the heating curves. It is surprising that the data correlate as well as they do.

3.3. Comparison between WAD and Other Methods. A comparison of the wax contents in whole crude oils and deposits by WAD and DSC shows a good correlation between the two methods (Table 6 and Figure 8a). However, the amounts by WAD are usually smaller than those by DSC because WAD detects only *n*-alkanes with carbon atoms above C_{20} that precipitate with MEK at -20 °C.[14] Pan et al.[20] showed that the lightest component that can be found in wax is *n*-C_{15}, which precipitates at -36 °C. Thus, the use of lower temperatures to precipitate waxes by WAD should be considered in future developments of this method. A closer analysis of the data indicates that the difference in wax content by the two methods is the smallest with waxy deposit 2 and the largest with Dagang crude oil. Characterization of these two samples is then undertaken using HTGC to investigate their composition. An initial separation to obtain a wax-rich fraction was not performed. Isomer information comes from a review of raw data, that is, area summations of components not in associated with the straight-chained hydrocarbon peaks. Figure 9 shows the *n*-alkane distribution of waxy deposit 2 and Dagang crude oil up to 100 carbon atoms. The distribution of branched alkanes is not shown here because it includes aliphatic chains in the asphaltene fraction. HTGC results in Figure 9a suggest that waxy deposit 2 contains *n*-alkanes with relatively low carbon number, with the maximum being at C_{30}. This possibly explains why the wax content by DSC and WAD are similar. On the other hand, Dagang crude oil contains a large proportion of *n*-alkanes with very high carbon atoms, which possibly are not fully soluble in heptane at 60 °C (see Figure 9b).[21] Also, DSC results can be dependent upon the amount of material analyzed, and Dagang oil has much higher wax content than other oils. This may explain the underestimated wax content by the WAD

method. Moreover, Dakota oil contains a significant amount of highly branched alkanes[1] that are not precipitated by MEK at -20 °C and thus are not detected as waxes by WAD.

The asphaltene amounts by WAD (see Table 4) compare well to the gravimetric data (see Table 1). Figure 8b shows a good correlation between the two methods, especially for samples with relatively low asphaltene content. The amounts by WAD are smaller than those by DSC for samples with higher asphaltene content, such as Minnelusa and Dagang crudes. This is because gravimetric *n*-heptane asphaltenes contain lower polarity material that elutes with the maltenes or oil fraction in the WAD separation method.

4. Conclusions

A separation called the WAD is successfully demonstrated using an initial precipitation of oil in MEK at -20 °C followed by sequential redissolution of precipitated component materials using heptane at -20 °C, heptane at 60 °C, toluene at ambient, and methylene chloride at ambient. This separation has the potential of measuring high-molecular-weight slightly to moderately branched alkanes and *n*-alkanes with carbon atoms above C_{20}, asphaltenes and polar asphaltenes in about 1 h using milligram quantities of oil. The amounts of asphaltenes separated by WAD compare well to the gravimetric data. After a comparison to DSC, it appears that the application of the WAD technique is ideal for petroleum fluids containing asphaltenes and relatively light macrocrystalline waxes. Further developments are currently being undertaken to characterize the chemical nature of material eluting under various peaks and to increase the applicability range of this technique and will be the subject of future reports.

(20) Pan, H.; Firoozabadi, A.; Fotland, P. Pressure and composition effect on wax precipitation: Experimental data and model results. *SPE Prod. Facil.* **1997**, *November*, 250.

(21) Jennings, D.; Weispfenning, K. Experimental solubility data of various *n*-alkane waxes: Effects of chain length, alkane odd versus even carbon number structure, and solvent chemistry on solubility. *Fluid Phase Equilib.* **2005**, *227* (1), 27–35.