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The effect of air blowing on the properties and constitution of a natural bitumen

SPEROS E. MOSCHOPEDIS, JAMES G. SPEIGHT
Fuel Sciences Division, Alberta Research Council, 11315–87 Avenue, Edmonton, Alberta, Canada

Air blowing of a natural and vacuum-reduced bitumen causes marked changes in the properties and constitution of the material. The products are harder and have higher softening points than the original material and the changes in physical properties appear to be related to the asphaltene content which increases with the temperature and duration of the blowing process. Analytical data indicate that conversion of the original resins to asphaltenes and the formation of new resins from the oils occur simultaneously; the data also provide feasible representations of the pathways of bitumen maturation and asphalt deterioration.

1. Introduction

Recent dramatic increases in world oil consumption and price have forced the petroleum industry towards less conventional sources of hydrocarbons for the production of products parallel to those from conventional crude oils. One of the largest such sources of hydrocarbons is the oil sand formation located in the Athabasca region of the province of Alberta. The oil sands, also variously referred to as tar sands or bituminous sands, were first reported in 1778 [1] and have attracted intermittent attention since well before the end of the 19th century but serious efforts to exploit them as sources of petroleum hydrocarbons are recent developments culminating in the commencement of the first commercial plant for the production of "synthetic" crude oil from the sands [2].

The bitumen extracted from the oil sands is a viscous material with a specific gravity of ~1.03 and a viscosity, at room temperature, of several thousand poises [3] and contains 40 to 50% wt/wt asphaltic materials, i.e. asphaltenes plus resins [4]. In fact, the composition and physical characteristics of the bitumen closely resemble those of asphaltic residues obtained as by-products from crude oil refining. However, one aspect of bitumen chemistry that has received comparatively little attention is the mechanism of oxidation reactions and the sequence of events leading to bitumen maturation and to asphalt deterioration. To date, only preliminary attempts have been made to resolve some of the unknown factors in the oxidation process by examining the influence of various oxidants on the bitumen. For example, in previous communications [5, 6] the effects of a variety of oxidizing agents on asphaltenes separated from the Athabasca bitumen were described, and the effects of oxygen at elevated temperatures (150 to 250° C) on other fractions derived from the bitumen have also been reported [4]. The results indicate that the predominant trend in the reactions with oxygen is the formation of more complex materials of higher molecular weight and oxidative degradation of the aromatic systems appeared to be of lesser significance. Bitumen oxidation with oxygen in the presence of a diluent [7] causes marked increases in asphaltene content with a noticeable reduction in asphaltene solubility. It is suggested that one of the main factors influencing asphaltene solubility, aside from possible polymerization reactions, is incorporation of oxygen groups during the oxidation process and consequent changes in polarity which are sufficient to influence asphaltene deposition. It seemed worthwhile, therefore, to pursue these investigations and to attempt to show what relationships, if any, exist between the physical consistency of the products and their chemical composition.

2. Experimental

Athabasca bitumen, obtained by the hot-water separation process and subsequently dried (Syncrude Canada Ltd) was used as-received.

2.1. Vacuum distillation of bitumen

A weighed amount of bitumen was placed in a long-neck 1000 ml round-bottom flask fitted with a condenser, and heated in an oil bath containing wax of high flash point. The bitumen was heated at the desired temperatures under 15 ± 3 mm, Hg pressure, until distillation of the light fractions ceased.

2.2. Air-blowing of bitumen

2.2.1. Method A

The residual bitumen from the vacuum distillation was further heated in a two-necked round-bottom flask at 260° C for 4 h, while air was bubbled through the bituminous mass at a rate of 2 to $3\,\text{cm}^3\,\text{min}^{-1}/\text{g}$ bitumen. These experiments were conducted without a reflux condenser and weight losses of 20 to 40% were recorded.

2.2.2. Method B

A known weight of bitumen was placed in a two-necked round-bottom flask and heated to the desired temperature. Air was then bubbled through the bitumen at a rate of 2 to $3\,\text{cm}^3\,\text{min}^{-1}/\text{g}$ bitumen. An air-cooled reflux condenser, which was further connected to a water-cooled condenser, was attached to the flask to collect any distillate. After completion of the air blowing, the samples were transferred into metal containers and fast-cooled.

2.3. Separation of bitumen components

Asphaltenes were separated by dissolution of the bitumen in an equal volume of benzene followed by dilution of the solution with 40 volumes of *n*-pentane whereby the precipitated asphaltenes were recovered by filtration. The filtrate, which contains the resins and oils, was chromatographically separated on Attapulgus clay which adsorbs the resins and then renders them insoluble in *n*-pentane; the resins were extracted with methyl ethyl ketone ("resins I") and tetrahydrofuran-water ("resins II"). The oil fraction was chromatographed into "saturates" and "aromatics" by means of an alumina–silica gel column and elution with *n*-pentane and benzene, respectively.

2.4. Physical properties

Elemental compositions were determined by the Alfred Bernhardt Microanalytical Laboratory, West Germany. Molecular weights were measured osmotically in benzene. Physical characteristics (i.e. penetration and softening point) of the natural bitumen and residua were measured by standard ASTM methods. Softening points of the asphaltene fractions were determined on a Buchi, Dr Tottoli, melting point apparatus.

3. Results

Inspection of the results presented in Table I shows that marked changes occur in the properties and constitution of a natural bitumen when the material is subjected to vacuum distillation and then to air blowing at 260° C. For example, the bitumen, which is originally too soft to record a penetration, gradually hardens, as anticipated, through removal of the light ends by distillation. This trend to a harder material continues when the residua are air-blown so that the ultimate product of air blowing is a hard material which has a penetration of 3. In keeping with the trend to a harder material, softening points gradually increase from 22° C in the natural material to a maximum of 87° C in the air-blown residuum (IV; Table I). It is also of interest to note the changes in composition which occur during these treatments and which can be associated with the changes in penetration and softening point. As expected, removal of the lighter ends by distillation causes a shift in composition to the heavier fractions and, accordingly, the residua have higher proportions of asphaltenes and resins than the natural material with a concurrent reduction in the proportions of saturates and aromatics. It is perhaps worthy of note here that the residua require approximately 60% wt/wt asphaltenes plus resins in order that a penetration number can be recorded. The trend to higher molecular weight materials is also evident after air blowing of the residua where asphaltene contents (17.4% wt/wt in the natural bitumen) in the range 28 to 46% wt/wt are recorded. However, air blowing causes some noticeable decreases in the proportions of resins present (especially the more polar resins II) whereas the proportions of saturates and aromatics are affected to a somewhat lesser extent. It is

TABLE I Physical Characteristics of bitumen, vacuum residua and air-blown vacuum residua

Starting material	T(° C) ($P = 15 \pm 3$ mm Hg)	Product distribution (wt %)		Residuum properties		Composition of residua (%)				
		Residuum	Distillate	Penetration (25° C, 100 g sec^{-1}) (5 sec)	Soft point (° C) R & B	Asphaltenes	Resins I	Resins II	Saturates	Aromatics
Natural bitumen	–	–	–	Too soft	22	17.4	24.0	3.35	24.5	30.8
Natural bitumen	260 ± 3	92.9 (I)	7.1	Too soft	23	21.5	28.1	5.40	18.4	26.6
Natural bitumen	320 ± 3	83.5 (II)	16.5	Too soft	31	21.5	30.8	6.82	15.8	25.1
Natural bitumen	350 ± 3	75.3 (III)	24.7	143	42	25.1	28.6	6.50	14.2	25.5
Natural bitumen	400 ± 3	50.0 (IV)	50.0	22	60	33.5	32.0	5.85	9.85	19.2
After air blowing (method A)										
Natural bitumen	260 ± 3			69	49	28.4	23.3	2.54	20.0	26.9
Residuum I	260 ± 3			46	53	32.3	23.1	2.13	18.1	25.1
Residuum II	260 ± 3			63	48	29.1	26.0	2.37	16.6	26.0
Residuum III	260 ± 3			25	59	31.3	26.3	3.19	14.5	24.8
Residuum IV	260 ± 3			3	87	46.1	28.7	2.90	5.7	16.6

evident that the proportion of asphaltenes in the bitumen or residua exerts considerable influence on the physical properties of the material and it is interesting to note that a vacuum residuum (IV, Table I) having 33.5%wt/wt asphaltenes has a penetration of 22 and a softening point of 60° C, whilst an air-blown residuum (III; Table I) with 31.3%wt/wt asphaltenes has remarkably similar data (penetration: 25, softening point: 59° C).

The analytical data recorded in Tables II to VI also present some indications of the chemistry of the air-blowing process. The majority of the oxygen within the natural bitumen and the products is distributed throughout the asphaltene and resin fractions with no detectable amounts occurring in the saturate and aromatic fractions. As anticipated, there is some oxygen uptake during the air-blowing process but the maximum recorded uptake (Table IV, residuum II) involves an increase of somewhat less than twice the atomic O/C ratio for this particular resin fraction relative to the O/C ratio of the natural resins. In most instances (Tables II to VI), oxygen uptake varies from 1.1 to 1.6 that of the natural materials, but it should be emphasized that the fractions (saturates and aromatics) in which oxygen was not detected prior to air blowing remained oxygen-deficient after the air-blowing process. Nitrogen and sulphur were found in all fractions and a surprisingly high amount of sulphur occurred in the

TABLE II Elemental analyses of asphaltenes from vacuum residua and air-blown vacuum residua

Source*	Composition (%)					Mol wt	Softening point range (° C)	H/C ratio	N/C ratio	S/C ratio	O/C ratio
	C	H	N	S	O						
Natural bitumen	79.52	7,91	1.60	7.97	3.00	4110	185–195	1.20	0.017	0.038	0.028
Residuum I	79.61	8.00	1.26	7.13	4.00	5104	175–185	1.21	0.014	0.034	0.038
Residuum II	79.96	8.00	1.54	7.08	3.42	5074	185–195	1.21	0.017	0.033	0.032
Residuum III	80.06	8.20	1.37	7.17	3.20	4650	185–195	1.22	0.015	0.034	0.030
Residuum IV	80.59	8.14	1.80	7.15	2.32	5163	220–230	1.21	0.019	0.033	0.022
After air blowing (method A)											
Natural bitumen	80.72	7.81	0.88	7.94	2.65	6380	195–200	1.16	0.009	0.037	0.025
Residuum I	80.15	7.82	0.85	7.62	3.56	6680	190–200	1.17	0.009	0.036	0.033
Residuum II	80.07	7.84	0.81	7.73	3.55	7074	185–195	1.17	0.009	0.036	0.033
Residuum III	80.40	7.93	0.86	7.67	3.14	6980	195–205	1.18	0.009	0.036	0.029
Residuum IV	82.30	7.31	0.95	7.10	2.34	6207	195–205	1.08	0.010	0.032	0.021

* See Table I for treatment conditions.

TABLE III Elemental analyses of resins I from vacuum residua and air-blown vacuum residua

Source*	Composition (%)					Mol wt	H/C ratio	N/C ratio	S/C ratio	O/C ratio
	C	H	N	S	O					
Natural bitumen	82.50	9.66	0.79	4.48	2.57	1247	1.40	0.008	0.020	0.023
Residuum I	82.05	9.88	0.74	4.56	2.77	984	1.45	0.008	0.021	0.025
Residuum II	82.98	10.02	0.63	3.96	2.41	986	1.45	0.007	0.018	0.022
Residuum III	81.88	9.86	0.73	5.43	2.10	1144	1.44	0.008	0.025	0.019
Residuum IV	82.82	9.52	0.74	4.60	2.32	924	1.38	0.008	0.021	0.021
After air blowing (method A)										
Natural bitumen	82.84	9.72	0.81	4.61	2.02†	913	1.41	0.008	0.021	0.018
Residuum I	80.71	9.61	0.83	5.19	3.66†	982	1.43	0.009	0.024	0.034
Residuum II	80.61	9.70	0.80	5.41	3.48†	989	1.44	0.009	0.025	0.032
Residuum III	80.71	9.62	0.94	5.24	3.49†	1070	1.43	0.010	0.024	0.032
Residuum IV	81.09	9.46	0.96	5.27	3.22†	836	1.40	0.010	0.024	0.030

* See Table I for treatment conditions.

† Oxygen determined by difference.

TABLE IV Elemental analyses of resins II from vacuum residua and air-blown vacuum residua

Source*	Composition (%)					Mol wt	H/C ratio	N/C ratio	S/C ratio	O/C ratio
	C	H	N	S	O					
Natural bitumen	81.52	9.88	0.83	4.30	3.47	1312	1.45	0.009	0.020	0.032
Residuum I	81.61	10.40	0.76	3.50	3.73	1046	1.52	0.008	0.016	0.034
Residuum II	81.12	10.20	0.91	4.26	3.51	1223	1.51	0.009	0.020	0.032
Residuum III	80.16	10.31	0.83	4.53	4.17	997	1.54	0.009	0.021	0.039
Residuum IV	81.70	10.17	0.83	3.54	3.76	820	1.49	0.009	0.016	0.035
After air blowing (method A)										
Natural bitumen	80.84	9.55	1.05	4.36	4.20	1672	1.42	0.011	0.020	0.039
Residuum I	79.98	9.94	0.80	4.71	4.57	1346	1.49	0.009	0.022	0.043
Residuum II	79.29	9.83	0.85	4.88	5.15	1048	1.49	0.009	0.023	0.049
Residuum III	80.28	9.86	1.00	4.83	4.03	1115	1.47	0.011	0.023	0.038
Residuum IV	81.11	9.53	1.03	4.77	4.56	1268	1.41	0.011	0.022	0.042

* See Table I for treatment conditions.

TABLE V Elemental analyses of saturates from vacuum residua and air-blown vacuum residua

Source*	Composition (%)				Mol wt	Refractive indices	H/C ratio	N/C ratio	S/C ratio
	C	H	N	S					
Natural bitumen	86.41	13.21	0.19	0.16	380	1.4820	1.83	0.002	0.001
Residuum I	86.44	13.22	0.18	0.12	423	1.4869	1.83	0.002	0.001
Residuum II	86.42	13.15	0.18	0.20	470	1.4900	1.82	0.002	0.001
Residuum III	86.39	13.23	0.21	0.13	499	1.4900	1.83	0.002	0.001
Residuum IV	86.39	13.20	0.15	0.26	601	1.4900	1.83	0.002	0.001
After air blowing (method A)									
Natural bitumen	86.42	12.73	0.14	0.55	913	1.4967	1.76	0.002	0.002
Residuum I	86.41	12.70	0.13	0.66	982	1.4970	1.76	0.002	0.002
Residuum II	86.50	12.81	0.12	0.52	+	1.4972	1.77	0.002	0.002
Residuum III	86.51	12.71	0.08	0.60	+	1.4989	1.76	0.001	0.002
Residuum IV	86.49	12.61	0.15	0.66	836	1.4985	1.75	0.002	0.002

* See Table I for treatment conditions.

\+ Insufficient sample.

TABLE VI Elemental analyses of aromatics from vacuum residua and air-blown vacuum residua

Source*	Composition (%)				Mol wt	Refractive indices	H/C ratio	N/C ratio	S/C ratio
	C	H	N	S					
Natural bitumen	84.10	10.00	0.17	5.73	383	1.5640	1.43	0.002	0.026
Residuum I	84.21	10.08	0.12	5.58	†	1.5642	1.44	0.002	0.025
Residuum II	84.02	10.01	0.22	5.73	420	1.5690	1.44	0.002	0.026
Residuum III	83.91	10.01	0.29	5.28	474	1.5680	1.43	0.003	0.026
Residuum IV	83.90	10.1	0.29	5.69	537	1.5685	1.44	0.003	0.026
After air blowing (method A)									
Natural bitumen	84.22	10.15	0.34	5.24	426	1.5760	1.43	0.003	0.023
Residuum I	84.09	10.11	0.48	5.28	427	1.5802	1.44	0.004	0.024
Residuum II	83.99	10.28	0.42	5.22	501	1.5691	1.45	0.004	0.023
Residuum III	84.37	10.11	0.20	5.28	531	1.5765	1.44	0.002	0.024
Residuum IV	84.34	10.30	0.24	5.10	552	1.5779	1.45	0.002	0.023

* See Table I for treatment conditions.

† Insufficient sample.

TABLE VII Physical characteristics of natural and air-blown bitumen (method B)

Blowing rate $2\text{–}3\ cm^3 min^{-1} g^{-1}$		Distillate (%) plus OH_2	Penetration 25° C, 100 g (5 sec)	Soft point (° C) R & B	Composition (%)		
T(± 2° C)	Time (h)				Asphaltenes	Resins	Saturates plus aromatics
–	–	–	Too soft	15	20.5	24.1	56.2
260	2	0.5	Too soft	15	20.6	24.8	54.6
260	6	1.8	249	38	29.7	25.5	44.5
260	8	1.0	238	27	25.3	25.8	48.9
260	24	7.3	16	92	45.2	23.7	31.5
290	6	2.7	233	38	32.0	22.6	45.4
290	12	9.4	36	70	42.1	25.8	32.0
290	24	10.9	14	86	45.0	25.1	29.2
320	2	6.4	Too soft	31	25.8	25.8	47.4
320	4	13.4	62	48	34.7	20.5	41.2

aromatics fractions (Table VII) and it appeared that the blowing process caused a decrease in nitrogen content of the asphaltenes (Table II).

Air blowing of the bitumen without prior removal of distillate again produced harder materials with decreased penetration and higher softening points (Table VII). At any given temperature, penetration decreased with time and the softening point of the product increased with time. Similarly, and as near as can be determined from the data, at any given time, penetrations decreased and softening points increased with temperature. Again, penetration and softening point of the product appeared to be related to the asphaltene content which increased with temperature and time. As the proportion of asphaltenes increased, the changes in the resin content were not so marked but substantial decreases were noted in the proportion of the saturates plus aromatics.

As before, the maximum recorded oxygen uptake (Table VIII; 260° C h^{-1}) involves an increase of somewhat less than twice the atomic O/C ratio for that particular fraction (in this case asphaltenes) and, in most cases, the oxygen uptake varies from 1.1 to 1.6 that of the natural material (Tables VIII to XII). Again, the saturates and aromatics, which contain little or no oxygen, were relatively oxygen-deficient after the air-blowing process. There is also the tendency to a reduction in oxygen content of the asphaltenes (Tables VIII) with duration of the blowing process and it may be suggested that this is due to initial introduction of oxygen as chemically labile functions, such as hydroxyl and/or carbonyl, which then undergo intra- or intermolecular condensation with elimination of the oxygen as water. In support of this, a reduction of the O/C ratio with duration of the blowing process is usually accompanied by an increase in recorded molecular weights of the asphaltenes. Some decrease in the nitrogen content of the asphaltenes was also noted (Table VIII), whilst air blowing caused more marked decreases

TABLE VIII Elemental analyses of asphaltenes from air-blown bitumen

Blowing rate $2\text{–}3\ cm^3 min^{-1} g^{-1}$		Composition (%)					Mol wt	Softening point range	H/C ratio	N/C ratio	S/C ratio	O/C ratio
T(± 2° C)	Time (h)	C	H	N	S	O						
–	–	80.31	8.59	1.14	7.97	1.99*	5600	190–200	1.28	0.012	0.037	0.019
260	2	80.25	7.96	0.93	7.98	2.88	8100	185–195	1.19	0.010	0.037	0.027
260	6	80.41	7.78	0.90	7.45	3.46	7620	200–210	1.16	0.010	0.035	0.032
260	8	80.30	7.75	0.77	7.47	3.71	7960	200–215	1.16	0.008	0.035	0.035
260	24	81.10	7.92	0.80	6.63	3.55	7435	> 265	1.17	0.008	0.031	0.033
290	6	81.96	7.99	1.20	5.95	2.90	7270	220–230	1.17	0.012	0.027	0.027
290	12	81.21	7.69	1.22	6.17	3.71*	3274	> 250	1.13	0.012	0.028	0.034
290	24	82.81	7.60	1.08	6.44	2.07	6400	> 265	1.10	0.011	0.029	0.019
320	2	80.22	7.77	1.18	7.24	3.59*	5150	185–195	1.16	0.013	0.034	0.034
320	4	81.48	7.52	1.27	6.85	2.88*	5600	220–235	1.11	0.013	0.032	0.027

* Oxygen determined by difference.

TABLE IX Elemental analyses of resins I from air-blown bitumen

Blowing rate 2–$3\ \mathrm{cm^3\,min^{-1}\,h^{-1}}$		Composition (%)					Mol wt	H/C ratio	N/C ratio	S/C ratio	O/C ratio
T(± 2° C)	Time (h)	C	H	N	S	O					
–	–	81.13	8.95	1.05	5.91	2.96*	1292	1.32	0.011	0.027	0.027
260	2	81.20	9.54	0.78	5.80	2.68*	925	1.41	0.008	0.027	0.025
260	6	80.23	10.43	0.86	5.54	2.94*	884	1.55	0.009	0.026	0.027
260	8	80.65	10.34	1.10	5.12	2.79*	895	1.53	0.012	0.024	0.026
260	24	81.16	9.66	0.67	4.54	3.97*	800	1.42	0.007	0.021	0.037
290	6	81.40	9.38	0.38	4.80	4.04*	712	1.38	0.004	0.022	0.037
290	12	84.31	9.69	0.37	4.21	1.42	631	1.38	0.004	0.019	0.013
290	24	83.10	9.53	0.49	4.60	2.28	781	1.37	0.005	0.021	0.021
320	2	81.11	9.36	0.53	4.68	4.32	970	1.38	0.006	0.022	0.040
320	4	81.12	9.36	0.48	4.57	4.47	910	1.38	0.005	0.021	0.041

* Oxygen determined by difference.

TABLE X Elemental analyses of resins II from air-blown bitumen

Blowing rate 2–$3\ \mathrm{cm^3\,min^{-1}\,h^{-1}}$		Composition (%)					Mol wt	H/C ratio	N/C ratio	S/C ratio	O/C ratio
T(± 2° C)	Time (h)	C	H	N	S	O					
–	–	79.77	9.70	0.99	4.81	4.73	2020	1.46	0.011	0.023	0.044
260	2	80.13	9.80	0.98	4.79	4.30	1050	1.47	0.010	0.022	0.040
260	6	80.93	9.98	0.88	4.22	3.99	1260	1.48	0.009	0.020	0.037
260	8	80.15	9.84	0.95	4.48	4.58	1260	1.47	0.010	0.021	0.043
260	24	79.76	9.94	0.80	3.84	5.66	750	1.49	0.009	0.018	0.053
290	6	79.64	9.71	0.50	4.47	5.68*	778	1.46	0.005	0.021	0.053
290	12	79.67	9.80	0.43	4.16	5.94*	522	1.47	0.005	0.020	0.056
290	24	79.30	9.93	0.63	4.27	5.87*	533	1.50	0.007	0.020	0.056
320	2	79.15	9.53	0.57	5.38	5.37*	935	1.44	0.006	0.025	0.051
320	4	79.56	9.62	0.48	4.41	5.93*	680	1.45	0.005	0.021	0.056

* Oxygen determined by difference.

TABLE XI Elemental analyses of saturates from air-blown bitumen

Blowing rate 2–$3\ \mathrm{cm^3\,min^{-1}\,g^{-1}}$		Composition (%)				Mol wt	Refractive indices	H/C ratio	N/C ratio	S/C ratio
T(± 2° C)	Time (h)	C	H	N	S					
–	–	86.94	12.65	0.03	0.33	370	1.4902	1.74	0.0003	0.001
260	2	86.92	12.68	0.02	0.38	369	1.4872	1.70	0.0002	0.002
260	6	86.68	12.95	0.04	0.33	394	1.4883	1.78	0.0004	0.001
260	8	86.81	12.91	0.02	0.26	398	1.4900	1.78	0.0002	0.001
260	24	86.96	12.74	0.04	0.26	400	1.4890	1.75	0.0004	0.001
290	6	86.80	13.00	nil	0.20	322	1.4879	1.79	–	0.001
290	12	86.45	13.03	0.03	0.49	406	1.4923	1.81	0.0003	0.002
290	24	86.43	13.00	nil	0.57	391	1.4912	1.80	–	0.002
320	2	86.61	13.08	nil	0.31	363	1.4857	1.81	–	0.001
320	4	86.42	13.01	nil	0.57	404	1.4938	1.80	–	0.002

TABLE XII Elemental analyses of aromatics from air-blown bitumen

Blowing rate 2–3 cm^{3}min^{-1}g^{-1}		Composition (%)				Mol wt	Refractive indices	H/C ratio	N/C ratio	S/C ratio
T(± 2°C)	Time (h)	C	H	N	S					
–	–	84.00	10.40	0.39	5.21	400	1.5770	1.48	0.004	0.023
260	2	84.40	10.28	0.25	5.08	378	1.5680	1.46	0.003	0.023
260	6	84.21	10.07	0.66	5.04	379	1.5678	1.44	0.007	0.023
260	8	84.70	9.69	0.23	5.38	408	1.5747	1.37	0.003	0.024
260	24	85.80	9.72	0.37	4.08	381	1.5748	1.36	0.004	0.018
290	6	85.71	9.97	nil	4.28	332	1.5706	1.39	–	0.019
290	12	85.70	9.70	nil	4.57	329	1.5807	1.36	–	0.020
290	24	85.62	9.74	nil	4.62	337	1.5810	1.36	–	0.020
320	2	86.05	9.89	nil	4.02	374	1.5672	1.38	–	0.018
320	4	85.54	9.81	nil	4.59	370	1.5794	1.38	–	0.020

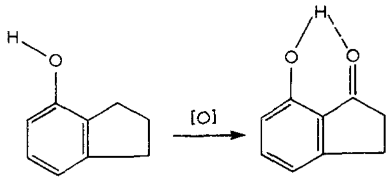
in the sulphur content of the asphaltenes (Table VIII), the resins (Tables IX and X), and the aromatics (Table XII).

4. Discussion

The results indicate that condensation to higher molecular weight material (e.g. asphaltenes; Tables I and VII) is one of the transformations which occurs during the blowing (oxidation) of bitumens at elevated temperatures and the overall low uptake of oxygen during this process suggests that its role is, presumably, little more than that of a catalyst for these condensation reactions. A cursory examination of the results indicates that the resin content remains relatively constant throughout the conversion of the bitumen, or vacuum residua, to the products but inspection of the H/C ratios of the resin fractions shows that the H/C ratios of the resins in the products are somewhat higher than those of the resins in the starting materials. It can only be concluded that this phenomenon arises by the formation of new resins, similar in nature and properties to the natural resins, from the oils but which are somewhat more aliphatic, i.e. higher H/C ratios.

It is also noteworthy here that the criteria for the formation of resin material from the saturates and/or aromatics may not only involve condensation of these entities to the higher molecular weight materials but also oxygen incorporation during the process. This would obviously alter the polarity of the "saturates" and "aromatics" to such an extent that they are then isolated as resins. Further work is proceeding in order to clarify this matter as other work has shown that asphalt oxidation is catalysed by the presence of inorganic materials [8]. Indeed, the valence state of the metal can influence the physical and chemical nature of the products to such an extent that asphaltene-type materials can be prepared from the oils (saturates plus aromatics) by air blowing under relatively mild conditions [9].

The mechanisms of bitumen oxidation are extremely complex and are largely speculative [7, 10] but, as expounded above, it does appear evident that condensation to higher molecular weight is one of the processes. Under the current conditions, some elimination of nitrogen and sulphur occurs with the distinct possibility that the eliminated sulphur may act as a condensing agent. However, one of the more important features of these reaction sequences is the incorporation of oxygen only into fractions, i.e. asphaltenes and resins, that already contain oxygen. This suggests activation of the ring systems, by the oxygen already present, to the incorporation of further oxygen functions:



Should this type of reaction occur during asphalt formation, or even during asphalt ageing, it could well have an adverse effect on asphalt stability. For example, it has been postulated several times and shown [11] that resins are responsible for the peptization of asphaltenes in the oily medium and, hence, the stability of heavy oils, bitumens and asphalts. One of the means by which the resins peptise the asphaltenes could well involve intermolecular hydrogen bonding [12] between the two. Should this situation be disturbed as, for example, by the incorporation of polar groups into, say, the asphaltenes, which can be accomplished by aerial oxygen [7], as in the manner outlined above, it is then feasible to assume that intramolecular hydrogen bonding will compete favourably with, and even supercede, the intermolecular hydrogen bonding ultimately resulting in depeptization of the asphaltenes and their deposition from the matrix.

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