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Battle River Coal Liquefaction and Its Co-Processing with Tar-Sand Bitumen

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Battle River coal from Canada shows an excellent applicability to liquefaction. At 450 °C, anthracene oil and Cold Lake tar-sand bitumen show the solvent effect as a vehicle oil in the initial stage of liquefaction. A definite advantage is gained by tar-sand bitumen co-processing, where hydrogen consumption is comparatively lower than that of anthracene oil derived from coal to produce a similar yield of oil.

As part of a study program of coals from the Pan-Pacific Basin area at the Government Industrial Development Laboratory, Hokkaido, their basic properties[1)] and their reaction characteristics in liquefaction[2,3)] have been studied. In a previous paper,[2)] the behavior during liquefaction of Wandoan coal, Australian subbituminous coal, was investigated. As to Battle River coal, Canadian subbituminous coal, the liquefaction test by a 0.1 T/D continuous plant was carried out.[3,4)] However, the detailed behavior during liquefaction is not sufficiently understood.

In the present paper, the reactivity in the liquefaction of Battle River coal from Canada was studied without vehicle oil and with tar-sand bitumen from Cold Lake, Canada, and anthracene oil derived from coal as vehicle oil in a batch autoclave in order to obtain fundamental data on the liquefaction and co-processing characteristics.

Experimental

The analytical data of Battle River coal, anthracene oil, and tar-sand bitumen are shown in Table 1. The experimental procedure and reaction conditions of coal liquefaction in a shaking-type, 500 ml autoclave are given in detail elsewhere.[2,5)] In the experiments of coal liquefaction, 10 g of Battle River coal, 1 g of a dry red-mud catalyst, 0.1 g of sulfur as a promoter, and 15 g of vehicle oil were charged in an authoclave. The initial pressure of hydrogen was adjusted to reach a reaction pressure of 220—230 kg cm^{-2}. The reaction temperature was 400 °C or 450 °C. Liquid and solid products were extracted with hexane and toluene successively, and they were separated into 3 fractions: a hexane-soluble fraction (oil), a hexane-insoluble/toluene-soluble fraction (asphaltene), and a toluene insoluble fraction (unreacted coal). The coal conversion was calculated on the basis of the unreacted coal.

Results and Discussion

Battle River coal (Fig. 1) and tar-sand bitumen (Fig. 2), were hydrogenated, respectively, with red-mud and sulfur without vehicle oil. In the liquefaction of the Battle River coal (Fig. 1), the conversion and the asphaltene yield at 400 °C tend to increase with an increase in the reaction time. The conversion reaches the equilibrium value at 450 °C, where the asphaltene yield decreases, and the gas yield, oil yield, and hydrogen consumption increase, with the increase in the reaction time. These results show that the secondary hydrogenolysis of the products occurs at 450 °C. Such a reaction trend is similar to that of Wandoan coal reported in a previous paper.[2)] However, the conversion of Battle River coal is 96 wt% daf at 450 °C and at 60—120 min, higher by about 3 wt% daf than that of Wandoan coal under the same reaction conditions.

The results of the hydrogenolysis of tar-sand bitumen itself as a blank run are shown in Fig. 2. As has been reported in a previous paper,[2)] the whole quantity of original anthracene oil is soluble in hexane, i.e., oil; hence, the whole quantity of the products after hydrogenolysis is also soluble in hexane. However, original tar-sand bitumen contains 15 wt% of the hexane insoluble/toluene soluble fraction, i.e., asphaltene. After hydrogenolysis, 3.3—

Table 1. Analysis of Sample Coal and Vehicle Oils

Coal and vehicle	Ultimate analysis/wt%					Atomic ratio		
	C	H	N	O	S	H/C	N/C	O/C
Battle River coal	70.0[a)]	4.7[a)]	1.7[a)]	23.1[a)]	0.6[a)]	0.80	0.021	0.247
Anthracene oil	90.0	6.2	1.1	2.4	0.3	0.83	0.011	0.020
Cold Lake tar-sand bitumen	83.7	11.4	0.3	0.6	4.0	1.64	0.003	0.005

a) d.a.f. coal basis. b) Proximate analysis of Battle River coal/wt%, Moisture: 11.9, Ash: 10.1, Volatile Matter: 34.1, Fixed Carbon: 43.3.

5.4 wt% of asphaltene remains in the products at 400 °C, while 0.6—2.1 wt% of asphaltene remains in the products at 450 °C. The hydrogen consumption is ca. 0.5 wt%[2] and is almost constant during the hydrogenolysis of anthracene oil, but when tar-sand bitumen is hydrogenated, the hydrogen consumption tends to increase with the increase in the reaction time; especially at 450 °C, it increases from 1 to 3 wt%. Regarding the gaseous products, the formation of hydrogen sulfide from tar-sand bitumen is remarkable and at 400 °C exceeds that of hydrocarbon gases, such as methane, ethane, and propane. No carbon monoxide or carbon dioxide formation was observed.

Figure 3 shows the results of the liquefaction of Battle River coal with anthracene oil and with tar-sand bitumen co-processing. The product yields are calculated as the difference between blank runs and those charged with coal. In this experiment, the effect of vehicle oil on the reactivity of the liquefaction of Battle River coal was examined. The conversion in the initial stage at 400 °C is about 30 wt% daf without vehicle oil (Fig. 1) and with tar-sand bitumen (Fig. 3), while it is about 80 wt% daf with anthracene oil (Fig. 3).

At 450 °C, the conversion, the asphaltene yield, and the oil yield in the initial stage up to the reaction time of 60 min show differences depending on the nature of the vehicle oil (tar-sand bitumen or anthracene oil) and on the presence or the absence of the vehicle oil. The effect of vehicle oil on the initial stage of liquefaction is clearly observed. Anthracene oil and tar-sand bitumen are different in the degree of the effect of vehicle oil in the initial stage; tar-sand bitumen contains more resins, asphaltene, and the heavy fraction boiling off above 400 °C, which should make it more viscous than anthracene oil, as is shown in Table 2. The fluidity of the reactants must be less in the initial stage when vehicle oil is tar-sand bitumen. Therefore, the reactivity of the reactants must be less.[6] However, as the reaction time and reaction temperature increase, the tar-sand bitumen decomposes (Fig. 2) and/or its viscosity must drop substantially. Therefore, as vehicle oil tar-sand bitumen shows an effect comparable to that of

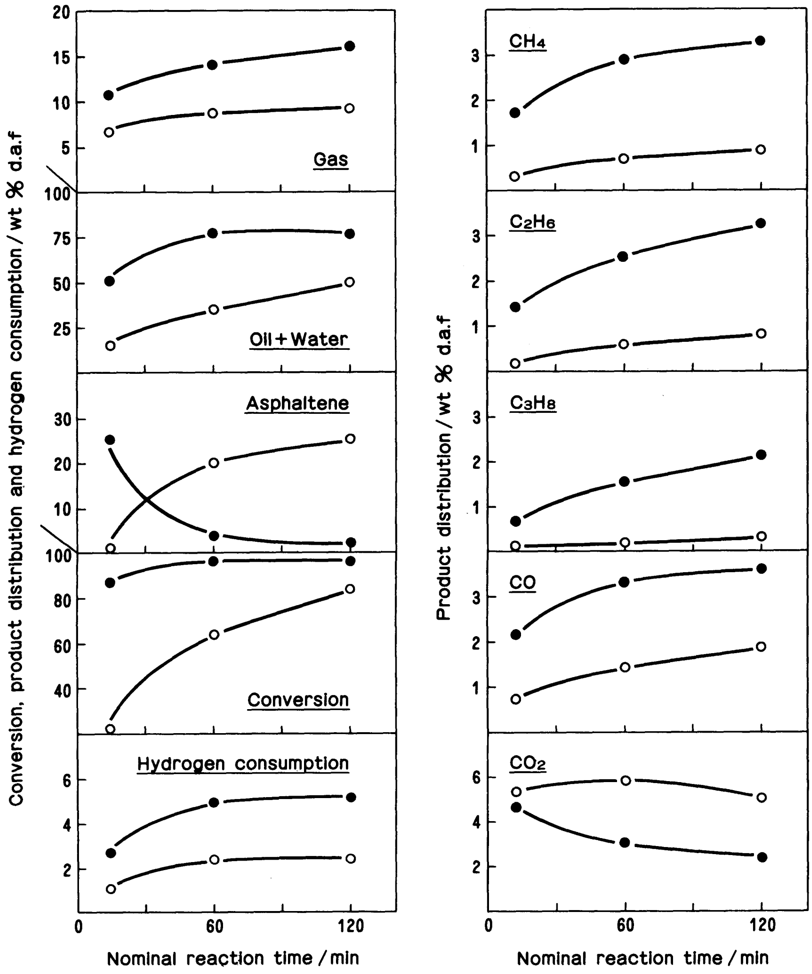

Fig. 1. Conversion, product distribution and hydrogen consumption vs. nominal reaction time on Battle River coal hydrogenolysis with red-mud/sulfur catalyst. ○: 400 °C, ●: 450 °C.

anthracene oil at 450 °C, as has been reported by Moschopedis.⑦ Hydrogen consumption and gas formation are the highest with anthracene oil, and they increase with an increase in the reaction time; subsequently, the oil yield tends to decrease. When tar-sand bitumen is used, the hydrogen consumption is lower and is considered to be the effect of hydrogen sulfide.[8-10] Hydrogen sulfide starts to decompose to hydrogen and sulfur above 400 °C, and it is easily decomposed to hydrogen and sulfur in the presence of iron sulfide.⑧ The hydrogen formed immediately after the decomposition of hydrogen sulfide can be more active than normal hydrogen, and the hydrocracking ability and the hydrogen-donor ability may play some role in the coal conversion.[8-10] The lower formation of gaseous products is remarkable.

In Table 3, the analytical data of the hexane-soluble fraction are shown. The hexane-soluble fraction in Table 3 is a mixture of the hexane-soluble fraction from Battle River coal and vehicle oil. In the presence of tar-sand bitumen, the hydrogen contents in the hexane-soluble fraction produced are higher than the

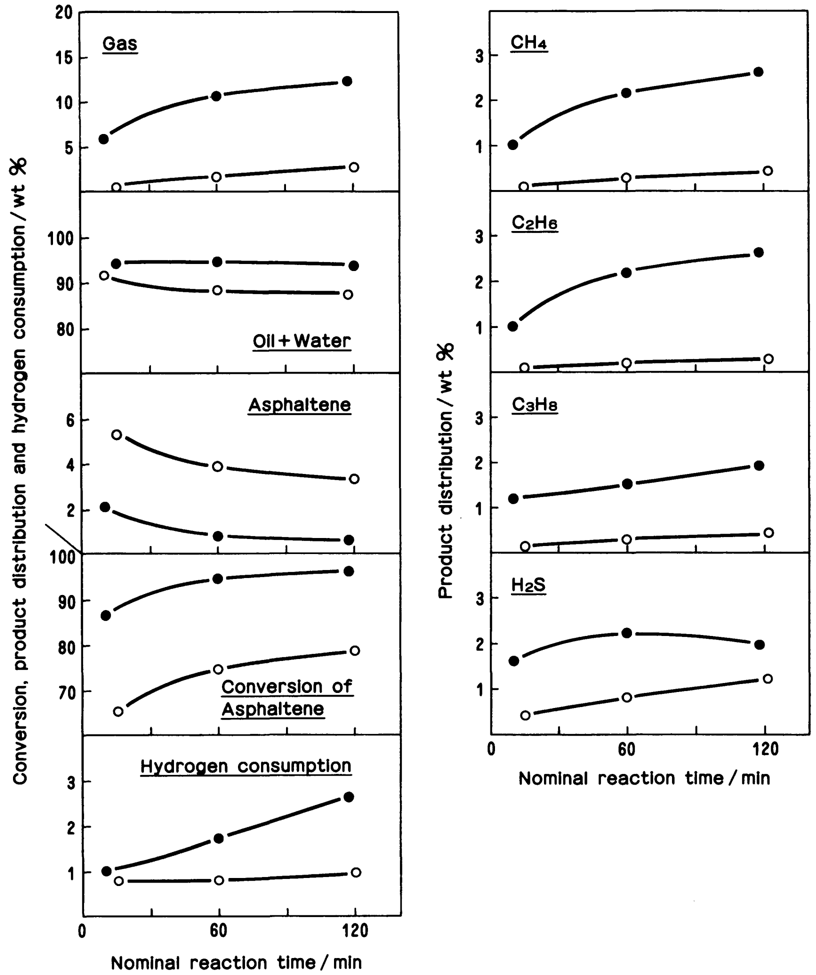

Fig. 2. Conversion, product distribution and hydrogen consumption vs. nominal reaction time on Cold Lake tar sand bitumen hydrogenolysis with redmud/sulfur catalyst. ○: 400 °C, ●: 450 °C.

Table 2. Analytical Data of Vehicle Oils

Vehicle oil	Type analysis/wt%				Boiling-range distribution/wt%			
	Saturated hydrocarbons	Aromatics	Resin	Asphaltene	Naphtha Fr. (IBP—200 °C)	Middle Fr. (200—325 °C)	Heavy Fr. (325—400 °C)	Residue (400 °C—FBP)
Anthracene oil	0.0	90.3	9.7	0.0	1.6	37.6	39.6	21.2
Tar-sand bitumen	18.3	56.2	10.5	15.0	1.6	46.0	24.3	28.2

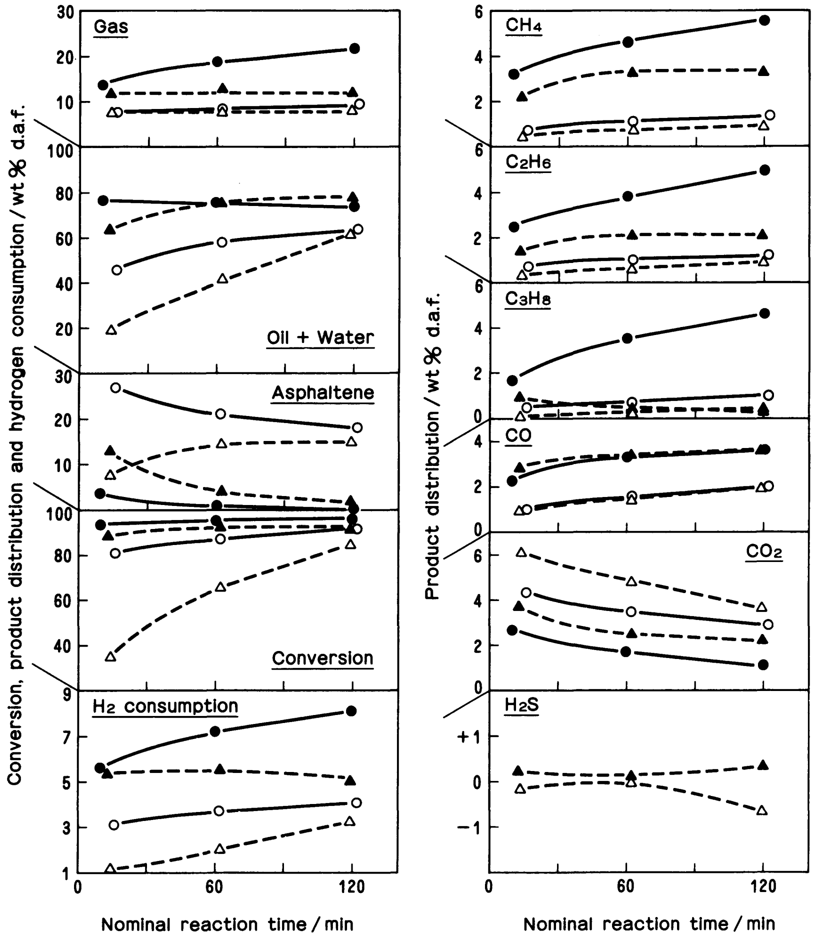

Fig. 3. Conversion, product distribution and hydrogen consumption vs. nominal reaction time on Battle River coal hydrogenolysis with red-mud/sulfur catalyst and anthracene oil and Cold Lake tar sand bitumen.
With anthracene oil, ○: 400° C, ●: 450 °C.
With Cold Lake tar sand bitumen, △: 400 °C, ▲: 450 °C.

Table 3. Analytical Data of Oil Produced from Battle River Coal

Reaction temp/°C	Reaction time/min	Ultimate analysis/wt%, d.a.f.					Atomic ratio			
		C	H	N	O	S	H/C	N/C	O/C	S/C
				Anthracene oil						
400	16	89.4	6.9	1.2	2.3	0.23	0.93	0.012	0.019	0.001
400	62	89.0	7.2	1.2	2.4	0.18	0.97	0.012	0.020	0.001
400	122	88.5	7.4	1.2	2.4	0.53	1.00	0.012	0.020	0.002
450	10	89.3	7.1	1.3	2.1	0.13	0.95	0.012	0.018	0.001
450	60	89.2	7.4	1.2	2.1	0.12	1.00	0.012	0.018	0.001
450	120	89.3	7.4	1.1	2.0	0.16	0.99	0.011	0.017	0.001
				Tar-sand bitumen						
400	14	83.7	11.1	0.63	1.1	3.4	1.59	0.006	0.010	0.015
400	62	84.3	11.0	0.81	1.4	2.5	1.57	0.008	0.012	0.011
400	119	84.8	10.9	0.76	1.4	2.2	1.54	0.008	0.012	0.010
450	13	85.4	10.3	1.0	1.5	1.7	1.45	0.010	0.013	0.007
450	62	86.2	9.8	1.0	1.5	1.5	1.36	0.010	0.013	0.007
450	119	86.2	9.7	1.1	1.6	1.5	1.35	0.011	0.014	0.007

hydrogen contents in the hexane-soluble fraction produced when anthracene oil was used. The H/C atomic ratio in the hexane-soluble fraction produced from co-processing with tar-sand bitumen is 1.4 to 1.6, higher by 1.4 to 1.7 times than the H/C atomic ratio in the hexane-soluble fraction produced when anthracene oil was used. Tar-sand bitumen seems to be associated with the lowering of the nitrogen content and the oxygen content in the hexane-soluble fraction. However, the sulfur in tar-sand bitumen was probably transferred to the hexane-soluble fraction.

Conclusion

In summary, Battle River coal shows an excellent reactivity to liquefaction, for the maximum conversion attainable is ca. 90 wt% daf at 400 °C and ca. 96 wt% daf at 450 °C. In the presence of anthracene oil as the vehicle oil, Battle River coal shows a liquefaction behavior similar to that of Wandoan coal. At 400 °C, anthracene oil is excellent as a vehicle oil to facilitate the liquefaction reaction during the heating period up to 400 °C. The conversion at 400 °C and 16 min reaches about 80 wt% daf. When tar-sand bitumen is used as the vehicle oil at 400 °C, the conversion shows a change, depending on the reaction time, similar to the conversion change in the case of no vehicle oil. Tar-sand bitumen shows the effect of vehicle oil on the increase in the oil yield. At 450 °C, anthracene oil and tar-sand bitumen show the effect of vehicle oil in the initial stage up to 60 min, and they facilitate the increase in the conversion and the oil yield and the decrease in the asphaltene yield. When tar-sand bitumen is used, it may be surmised that the conversion of tar-sand bitumen itself proceeds and that, at the same time, the conversion of coal-derived asphaltene to the oil fraction is also facilitated at 450 °C.

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