

LIQUEFACTION KINETICS INFLUENCED BY THE AMOUNT OF DONORS AND HYDROGEN PRESSURE

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Abstract

Influences of donor and solvent amounts, hydrogen pressure and coal deashing on the product slate as well as rates of liquid production were studied in the hydrogen donating liquefaction of an Australian brown and a Japanese subbituminous coal using tetrahydrofluoranthene(4HFL) as a donor at 450 °C. An adequate amount of donor at the fixed solvent/coal ratio provided the best yield of oil plus asphaltene. The best amount varied, depending upon the coal and liquefaction conditions. Less amount of donor at the decreasing solvent/coal ratio gave much rapid decrease of the liquid yield. Hydrogen pressure around 40 kg/cm² certainly participated favorable in the liquefaction, especially pronounced at the low donor/coal ratio as observed with pyrolyses of model substrates. Deashing to remove dominant calcium ions was generally favorable to increase the liquid yield, however some coals at the low donor/coal ratio suffered some retrogressive reaction. Such results indicate multi-fold roles of solvent and plural mechanisms of coal-macromolecular depolymerization. Different reactivities of the brown coals of different lots are briefly discussed.

Introduction

Coal liquefaction process has been investigated for quite a time by examining various ideas to improve its efficiency[1-5]. Nevertheless, the process is still far away from satisfaction about the cost of product oil. Better yield of distillate oil on the bases of reactor volume, hydrogen consumption and very severe reaction conditions as well as fed coal is desperately wanted.

The macromolecular mixtures of solid coal are digested and/or depolymerized into distillable species through solvent extraction as well as pyrolytic, hydrogen-transferring and catalytic bond dissociations[6]. Poor interaction between the solid coal grain and solid catalyst, unless the fine catalysts are highly dispersed on the coal with rather extensive cost[7,8], suggests that the first step of coal conversion to obtain liquid easily accessible to the solid catalyst is dominated by the reactions among coal molecules, the solvent and gaseous atmosphere. It has been pointed that hydrogen donor solvents derived from 3-4 ring aromatic hydrocarbons are very powerful to liquefy the coal through their proper hydrogen-donating and dissolving abilities against coal molecules[9,10]. Thus, most appropriate use of donor solvent is an approach to find better scheme of coal liquefaction. The minimum amount of donor solvent to assure the maximum yield of oil and asphaltene may increase the efficiency of hydrogen consumption and the reactor volume, and moderates the conditions[11].

In addition to a classical mechanism of stabilization of thermally produced radicals from coal molecules, it has been recognized that donor molecules directly interact with the coal macromolecules to activate via hydrogenation and hydrocracking according to the reactivity of coal molecules as well as the donor, and reaction conditions[6, 11-13]. Such bimolecular mechanisms suggest the importance of the solvent quality and quantity under reaction conditions matched to the both materials for the liquefaction efficiency.

The hydrogen transferring mechanism may also suggest the importance of hydrogen pressure when the molecular hydrogen is activated by the radical species derived from donors and coal molecules. Vernon has pointed out the participation of molecular hydrogen in the pyrolysis of dibenzyl with the existence of tetralin[14]. The radical initiator is also suggested important to initiate the chain reactions of coal and solvent molecules according to the bimolecular mechanism.

In the present report, we are going to describe the influences of donor concentration in the solvent, donor amount and hydrogen pressure in the liquefaction of an Australian brown and a Japanese subbituminous coal on the yield of oil and asphaltene which are both easily converted into distillable clean oil by the successive catalytic hydrotreating process. Influences of such reaction variables were also studied with model substrates. The reactivity of the coals is very sensitive to the coagulation of their macromolecules and maceral composition[15]. Hence, the influence of deashing on the hydrogen-donating liquefaction and microscopic coal characterization were investigated[16,17]. Morwell brown coal is found to exhibit very different reactivity according to the rot, yielding variable amounts of asphaltene and residue.

Experimental

Materials

The ultimate analyses of the sample coals are summarized in Table 1. The liquefaction(hydrogen donating) solvent was tetrahydrofluoranthene(4HFL) prepared by catalytic hydrogenation of commercial fluoranthene(FL) using a commercial Ni-Mo catalyst in an autoclave at 250 °C, and quantified by g.c. and purified by recrystallization.

Pretreatment of coal

After the coal was ground to pass 60 US mesh screen, it was kept in refluxing aq. HCl(1N) and methanol(10 vol%) under nitrogen flow to remove divalent cations such as Ca^{2+} , Mg^{2+} and Fe^{2+} . After the pretreatment, the coal was filtered, washed with water, and dried in vacuum at room temperature.

Liquefaction procedure

Liquefaction was carried out in a tube bomb(20 ml volume). The coal(2.0 g), which had been ground to less than 60 US mesh and dried at 100 °C under vacuum, and the solvent(2.0, 3.0, 4.0 or 6.0 g), after their thorough mixing, were transferred to the bomb. The bomb was then pressurized with nitrogen or hydrogen gas to 1.0 or 2.0 MPa at room temperature and immersed into a molten tin bath at the prescribed temperature, and agitated axially. The

products remaining in the bomb were extracted with THF, benzene and n-hexane. The hexane soluble(HS), hexane insoluble-benzene soluble(HI-BS), benzene insoluble-THF soluble(BI-THFS) and THF insoluble(THFI) substances were defined as oil, asphaltene, preasphaltene and residue, respectively. Gas yield was calculated by the difference between the initial and recovered weight.

Results

Influences of 4HFL concentration in the fixed solvent/coal ratio of 3/1

Influences of 4HFL concentration on the product slate in the liquefaction of Morwell-I coal at 450 °C under nitrogen were shown in Table 2. The pure 4HFL solvent liquefied the coal very rapidly, whereas a longer reaction time increased markedly the gaseous product as well as the sum yield of oil and asphaltene. Although decreasing 4HFL in the solvent reduced the rates of liquefaction as for both gas and liquefied products, the 4HFL contents of 3/4 and 2/4 in the solvent provided more favorable product slates(high yield(>80%) of oil plus asphaltene and low yields of preasphaltene and gaseous products).

Influence of 4HFL(solvent)/coal ratio

Figure 1 illustrates the oil and asphaltene yields from Morwell-I coal at 450 °C under nitrogen for the respective best residence times using variable solvent(pure 4HFL)/coal ratios. The oil and asphaltene yields were only slightly influenced by the ratios to give around 60 and 10 % yields, respectively, when the ratio ranged from 3/1 to 1.5/1, although a trend of slight decreases of both yields may be observable with decreasing the ratios. It is of value to point that the yields of preasphaltene and residue were always less than 5 %.

A drastic decrease of oil and hence the sum yield took place when the solvent/coal ratio was reduced to 1/1, while the significant increase of asphaltene with some increases of preasphaltene, residue and gas were observed at the best residence time of 10 min. The large increases of the latter three products were observed by a longer residence time at this ratio, resulting in a further marked decreases of objective products.

Influence of hydrogen pressure on coal liquefaction

Figure 2 illustrates the liquefaction yields from Morwell-I and -II coals at 450 °C and 1.5/1(4HFL/coal ratio) under nitrogen or hydrogen pressure. The conversion of asphaltene into oil was accelerated by hydrogen pressure, especially under higher pressure, where the interaction of molecular hydrogen with donor and/or coal molecules was enhanced. It should be noted that the highest oil yield from Morwell-II was achieved under higher hydrogen pressure at the reaction time of 20 min, when most of 4HFL was consumed.

Morwell-I was certainly more reactive than Morwell-II, giving higher oil yield regardless of atmosphere, although the sum yields of oil plus asphaltene were much the same. Lower reactivity of the asphaltene from Morwell-II coal is suggested.

Figure 3 illustrates the liquefaction yields from Taiheiyu

coal at 450 °C and 1.5/1(4HFL/coal ratio) under nitrogen or hydrogen pressure. Higher oil and asphaltene yield of 80 % was achieved from Taiheiyō coal than Morwell coals, reflecting much less gas yield. Pressure effect of hydrogen was marked at the reaction of 10 min, converting asphaltene into oil.

Influence of hydrogen pressure on the reaction of model compounds

Table 3 summarizes the influence of hydrogen pressure on the conversions of dibenzyl (DB) at 450 °C, 30 min and variable donor(4HFL)/substrate ratios. The conversions of DB were always higher under hydrogen pressure with less 4HFL consumption than those under nitrogen pressure. Such a tendency increases with decreasing 4HFL amount. It should be noted that hydrogen pressure enhanced the DB conversion even with a non-donor solvent.

Influence of deashing at low 4HFL/coal ratio

Figure 4 illustrates the liquefaction yields from the deashed Morwell-I and Taiheiyō coals at 450 °C-10 min and 1.5/1 (4HFL/coal ratio). The oil yield from Morwell-I coal increased to 65 % with decreasing gas, preasphaltene and residue yields. In contrast, the deashing pretreatment exhibited unfavorable effect on the liquefaction of Taiheiyō coal at low 4HFL/coal ratio, increasing the yields of gas and heavy fractions (preasphaltene and residue) with slight increase of oil yield.

Discussion

The present study revealed that the concentration and amount of donor, and hydrogen pressure are very influential on the yield of oil plus asphaltene in the hydrogen-transferring liquefaction. The volume of solvent defines the volume of reactor and its reduction can increase the productivity of the liquefaction.

The roles of solvent have been recognized multi-fold. The hydrogen donation performs the following reactions in coal liquefaction;

1. Stabilization of radicals derived thermally from the coal molecules.
2. Hydrogenation of reactive sites of coal molecules to loosen the bonds for their dissociation.
3. Cleavage of bonds in coal molecules by substitution with hydrogen atoms.

The contributions of these schemes are strongly dependent upon the reactivities of coal and solvent, and hence reaction conditions[11].

According to scheme 1, the coal liquefaction requires donor solvent over a certain quantity. Its excess amount stays unparticipated. Less amount fails to prevent the retrogressive reaction. In contrast, according to the schemes 2 and 3, the donor directly reacts with the coal molecules. Hence, its amount kinetically influences the liquefaction, more amount accelerating the rate of liquefaction. Such schemes certainly depolymerize the coal molecules into oil and asphaltene directly or indirectly through preasphaltene, but also accelerate the gas

formation through the hydrocracking of alkyl side-chains and naphthene rings. Thus, the optimum amount of donor exists to produce the maximum yield of oil plus asphaltene. The optimum amount may vary due to the coal, donor and reaction conditions which are all influential upon the participation extent of the schemes. The present study certainly indicates the optimum amount of the donor for the maximum yield. Taiheiy coal required more donor for the production of oil than Morwell-I coal. Larger extent of depolymerization is required with higher rank coal.

The solvent is expected to play roles of dissolving and dispersing agents against coal-derived molecules and donor. Their intimate contact and radical dispersion which are strongly influential on the liquefaction as well as retrogressive reactions are assured by the solvent. Hence, the amount of non-donor solvent participates the liquefaction scheme. The difference between the same amounts of the donor in the fixed amount of aromatic solvent and alone without additional solvent is thus definite, although smaller amount of solvent may be favorable when the product slate is acceptable.

The optimum amount of donor can be reduced under the hydrogen pressure if the hydrogen is transferred to the donor, coal molecules or radicals derived from donor and coal molecules. Vernon has indicated the participation of molecular hydrogens in the pyrolysis[14]. The present results indicate that it is possible with certain types of model molecules and coals. Such a participation of molecular hydrogen under some pressures may reduce the difficulty of catalytic hydrotreating process of the second stage, where the hydrocracking for more oil and hydrogenation for the solvent regeneration are both expected. The first stage requires some pressure in any case to maintain the solvent in the liquid phase and coal-derived molecules.

The deashing for some coals has been reported to increase the yield of liquid product in the hydrogen transferring liquefaction with sufficient amount of solvent through enhanced fusibility via liberation of coal macromolecules[11]. It is not always the case when less amount of solvent is applied. Larger amount of donor may be necessary at a time to match the enhanced reactivity of deashed coal. Morwell-II coal exhibited certainly less reactivity and influence of deashing. The marked difference is found in the conversion of asphaltene to oil. More unreactive asphaltene is presented in the product from Morwell-II coal. Detail structure of asphaltene is an objective of future study. Taiheiy coal exhibited little influence of deashing, especially with smaller amount of donor solvent.

The combination of deashing pretreatment and hydrogen pressure is of value for study to obtain higher yield of oil and asphaltene by reducing the preasphaltene and residue, since the deashing pretreatment is expected to simplify the liquefaction steps and solve the operational problems[18].

The amount of solvent can be hopefully reduced to the level which is necessary for coal slurry transportation, which requires a significant amount of liquid at room temperature. Such a vehicle solvent is not needed any more when a certain extent of liquefaction has proceeded to supply the solvent fraction. The

removal of such lightest portion in the solvent can economize the reactor volume.

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Table 1

Elemental analyses of sample coals

Coal name	wt% (daf)				Ash (wt%)
	C	H	N	(O+S)	
Morwell-I	60.5	5.5	0.5	33.4	2.4
Deashed-I	61.2	5.4	0.5	32.9	1.1
Morwell-II	63.7	4.9	0.6	30.8	2.3
Taiheiyo	73.5	6.3	1.2	19.0	17.3
Deashed coal	73.9	6.3	1.3	18.6	10.9

Table 2

Influences of donor(4HFL) concentration in the solvent¹⁾
on the liquefaction yields from Morwell-I coal at 450 °C

4HFL (%)	Reaction time(min)	Yield (wt%)				
		Gas	Oil	Asph.	Preasph.	Residue
100	5	19	56	13	12	0
	20	20	62	14	4	0
	30	28	53	14	5	0
75	5	13	51	15	15	6
	20	14	68	14	4	0
	30	13	68	14	5	0
50	5	6	50	23	14	7
	10	10	56	19	6	9
	30	9	60	22	6	3
25	5	8	44	21	12	15
	10	8	47	18	14	13
	30	10	48	17	7	18

1) Solvent/coal ratio = 3/1(fixed)
Solvent composition : 4HFL/(4HFL+FL)
(FL: fluoranthene, 4HFL: tetrahydro-FL)

Table 3

Influence of hydrogen pressure on dibenzyl(DB)
conversion at 450 °C-30 min

Atmosphere ¹⁾ (kg/cm ²)	Reactants (mmol)			Conversion(%)	
	DB	FL	4HFL	DB	4HFL
N ₂ (10)	2.75	14.9	0	25	-
H ₂ (20)	2.75	14.9	0	36	-
N ₂ (10)	2.75	14.6	0.24	25	100
H ₂ (20)	2.75	14.6	0.24	33	76
N ₂ (10)	2.75	14.4	0.49	32	85
H ₂ (20)	2.75	14.4	0.49	38	58

1) (): initial pressure

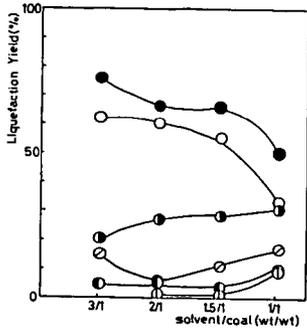


Fig. 1
Influence of solvent (4HPL)/coal ratio
on the liquefaction yields at 450°C

●: (oil+asphaltene), ○: oil, ●: gas, ○: asphaltene,
●: preasphaltene, ○: residue

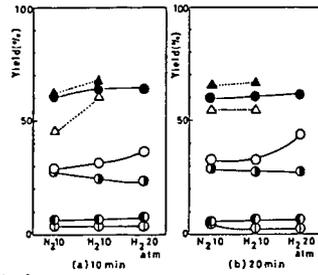


Fig. 2
Effects of hydrogen pressure on the liquefaction of
Morwell-I and -II coals at 450°C, 1.5/1 (solvent/coal)

Morwell-I ▲: O+A, △: O
Morwell-II ●: O+A, ○: O, ●: G, ○: P, ○: R

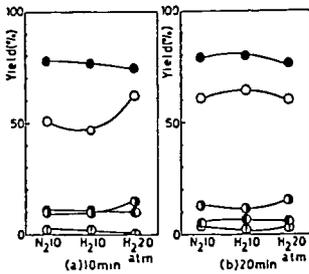


Fig. 3
Effect of hydrogen pressure on the
liquefaction of Taiheiyu coal at 450°C
and 1.5/1 (solvent/coal)

●: (O+A), ○: O, ●: G, ○: P, ○: R

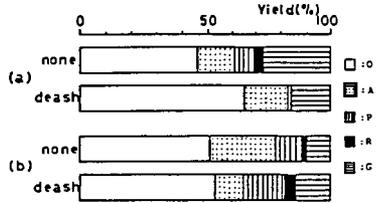


Fig. 4
Effect of deashing on the liquefaction at
450°C-10 min (solvent/coal=1.5/1, solvent:4HPL)

(a) Morwell-I (b) Taiheiyu