

## Co-liquefaction of Enriched Coal Maceral Constituents and Sawdust

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**Abstract:** Co-liquefaction of coal and sawdust was studied in the presence of hydrogen-donor solvent, tetralin. Coal samples were prepared through floatation of the Xinwen coal, followed by enrichment of maceral constituents. Sample I was rich in vitrinite and Sample II fusinite. Effects of reaction temperature, time and initial cold H<sub>2</sub> pressure were studied on conversion, yield, especially oil yield, through comparison between these two samples. Because it is more difficult to be liquefied, Sample II, is greatly affected by changes in temperature and time. However, it is almost independent of change in initial cold H<sub>2</sub> pressure, owing to the role of tetralin as hydrogen vehicle. Certain product(s) formed from thermolysis of sawdust can help hydrogenation of the intermediate (asphaltene and preasphaltene) in further forming oil products.

**Key words:** co-liquefaction; coal; vitrinite; fusinite; sawdust

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### 1 INTRODUCTION

Coal is an important fossil fuel, with a huge reserve widely spread on the earth<sup>[1]</sup>. Biomass belongs to the renewable energy source that comes from conversion of solar energy by plants. The efficient utilization of these two types of energy resources is of great significance for sustainable development of human society. Since 1970s, research on coal liquefaction has been focused on development of new technologies, catalysts and reactors, and remains attractive in terms of future prospect.

It is reported that co-liquefaction of sawdust and coal can reduce the severity of liquefaction conditions, meanwhile improve oil yield<sup>[2-4]</sup>. Further investigations indicate that substances of phenol derivatives in lignin help breaking ethereal bonds in the chemical structure of coal and thus promote the formation of products containing smaller molecules.

Coal itself is a complicated matter due to inter-links among compounds that are somewhat similar but not identical in chemical structure. Different macerals of coal display different readiness in liquefaction and lead to different results under the same conditions. In this paper, investigation was made on liquefaction behaviors of samples prepared from coal washing that separates the coal into two portions enriched either in vitrinite or in fusinite. On the basis of the previous study on co-liquefaction of sawdust and crude coal<sup>[5]</sup>, liquefaction behaviors of individual maceral-enriched samples with sawdust in response to reaction time, cold hydrogen pressure and reaction temperature were examined.

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## 2 EXPERIMENTAL

### 2.1 Test Materials

Maceral constituents of the Xinwen coal (Shanxi Province, China) are listed in Table 1.

**Table 1 Analysis of maceral constituents of the Xinwen coal (% ,  $\omega$ )**

Vitrinite	Exinite	Fusinite	Mineral	$R_{\max}$
78.2	3.2	16.6	2.0	0.75

$R$  is an index in the analysis of maceral constituents of a coal sample. It is defined as the ratio of the intensity of reflected light from the surface of the measured maceral constituent to the intensity of the incident light onto the surface.

With the liquid mixture of water, kerosene and sec-octanol as floatation medium, coal was separated into three parts(in Table 2): Sample I, moisture 3.10%( $\omega$ ), ash(dry) 7.45%( $\omega$ ), enriched by vitrinite maceral (94.5%,  $\omega$ ), Sample II, moisture 3.07%( $\omega$ ), ash(dry) 8.57%( $\omega$ ), enriched by fusinite maceral (58.8%,  $\omega$ ), and residue sawdust with the characteristic data shown in Table 2.

**Table 2 Analysis of sawdust (% ,  $\omega$ )**

Moisture	Ash (dry)	Extract by hot water <sup>1)</sup>	Semi-cellulose <sup>1)</sup>	Cellulose <sup>1)</sup>	Lignin <sup>1)</sup>
9.94	4.03	5.90	13.24	43.85	41.74

Note: 1) Dry and ash-free.

### 2.2 Experimental Apparatus and Method

The experimental apparatus was an autoclave manufactured by Autoclave Engineering Inc., USA, with a volume of 300 ml, designed pressure 34.3 MPa and max. operation temperature 783 K. The autoclave was equipped with an electro-magnetic stirrer, a cooling coil and a TDK-702 temperature controller.

Each run of tests started when the autoclave was filled with cold hydrogen up to the desired pressure and then heated at the rate of 10°C/min. Reaction timer was triggered as the mass was heated to the desired temperature. During the operation, the stirrer speed was kept at 1000 r/min. When the reaction came to stop at the specified time, the whole lot in the autoclave was quenched. Both gas(G) and liquid products were sampled for analysis. Of liquid products, the part that is soluble in tetrahydrofuran but insoluble in *n*-hexane is defined as asphaltene and preasphaltene(A) while the part soluble in the both solvents defined as oil(O).

## 3 RESULTS AND DISCUSSION

### 3.1 Comparison among Liquefaction of the Two Samples and Crude Coal

It is quite evident from Table 3 that under the same operation conditions, the order of Sample I >crude coal>Sample II exists on the basis of values of conversion ( $X$ ), oil yield ( $Y$ ) and hence the selectivity ( $S$ ) that is calculated from the definition of  $S = Y/X$ . It can also be seen that Sample I is the easiest one for liquefaction. This difference in the results becomes comparatively evident at lower temperatures, but along with the increase in temperature, this difference abates.

This phenomenon can be explained by the kinetic model<sup>[6]</sup> in which the assumption on the normal distribution of activation energies of the complicated reactions accounts for not only the complicated chemical structure of coal but also the readiness of liquefaction for individual constituents.

As for Sample I, the vitrinite maceral has higher chemical activity, i.e., lower activation energy than fusinite maceral. The fact that oil selectivity varies significantly at lower temperature while the change becomes moderate at higher temperature implies that the intermediate products, asphaltene and preasphaltene, have higher activation energies in the consecutive reactions.

**Table 3 Comparisons of liquefaction results under different temperatures**

Temp. (°C)	Conversion (% , $\omega$ )			Oil yield (% , $\omega$ )			Selectivity (% , $\omega$ )		
	Sample I	Crude coal	Sample II	Sample I	Crude coal	Sample II	Sample I	Crude coal	Sample II
350	52.49	40.2	35.04	2.15	0.0	0.76	4.1		2.17
380	66.81	62.1	59.93	7.37	4.1	0.93	11.0	6.6	1.55
400	75.21	73.6	71.70	16.14	11.2	12.35	21.5	15.2	17.2
420	81.75	78.0	77.13	27.13	26.0	23.18	33.2	33.3	30.0

Reaction conditions: sample 20 g, tetralin 60 ml, reaction time 30 min.

### 3.2 Co-liquefaction with Sawdust

#### 3.2.1 Effect of addition of sawdust

Sawdust is very easy to be liquefied at the temperature around 200°C under the initial cold hydrogen pressure of 3.40 MPa, and the conversion reaches over 90% ( $\omega$ ) with oil yield 24% ( $\omega$ ) in half an hour<sup>[5]</sup>. Data from co-liquefaction of individual samples with sawdust are listed in Table 4.

**Table 4 Advantages from co-liquefaction with sawdust (% ,  $\omega$ )**

Coal	Conversion	Yield of asphaltene and preasphaltene	Oil yield	Gas yield
Sample I	66.81	57.31	7.37	2.12
Sample II	59.93	56.82	0.93	2.17
Crude coal	62.10	58.00	4.10	0.00
Sample I + sawdust	79.11	36.05	34.94	8.12
Sample II + sawdust	74.51	55.65	9.28	9.58
Crude coal + sawdust	80.00	40.00	25.00	15.00

Reaction conditions: 20 g sample, 50% share of each material if in co-liquefaction test, tetralin 60 ml, reaction time 30 min; cold hydrogen pressure 3.40 MPa, reaction temperature 380°C.

From the conversion data alone, if calculations made were on the basis of the share of either coal or sawdust, the addition of sawdust by no means can make any contribution in promotion of the overall conversion. However, from the data of oil yield, if compared with the calculated values on the share of each material, it can be concluded that some products formed from thermolysis of sawdust help hydrogenation of asphaltene and preasphaltene so that oil yield is improved. The oil yield from co-liquefaction of Sample I can be 8.7% higher than the value calculated on the basis of individual share of the materials, 2.3% higher in the case of crude coal and sawdust, but at least 10% lower for Sample II and sawdust while gas yield is consistent with the contribution by sawdust share.

#### 3.2.2 Effect of reaction temperature

In the temperature range from 350°C to 420°C, investigation was made on the co-liquefaction of sawdust with Samples I and II. In Figs.1 and 2, it can be seen that with increasing temperature, the increase in conversion for Sample I (from 72% to 80%) is smaller than that for Sample II (from 50% to 80%); the same as in the case of oil yield, i.e., from 28% to 39% for Sample I and from 0.5% to 20% for Sample II. This suggests that vitrinite maceral in Sample I is readily to be thermally decomposed at lower temperatures into asphaltene and preasphaltene, which are consecutively turned into oil through hydrogenation promoted by the products from thermal decomposition of sawdust. For this reason, there will be no obvious variations in the yield of

asphaltene and preasphaltene within the temperature range, and at the same time, only a slow increase in oil yield can be observed. On the contrary, for fusinite maceral in Sample II, only at a higher temperature can it be significantly decomposed, and therefore, the yield of asphaltene and preasphaltene shows a maximum value while oil yield increases monotonously in the medium temperature range.

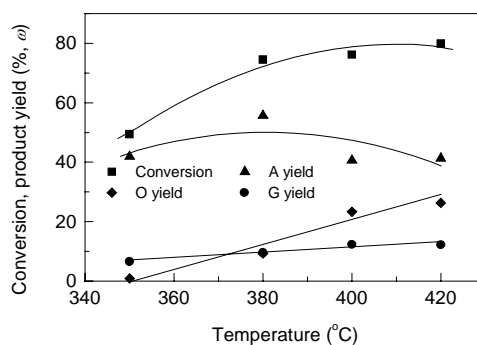
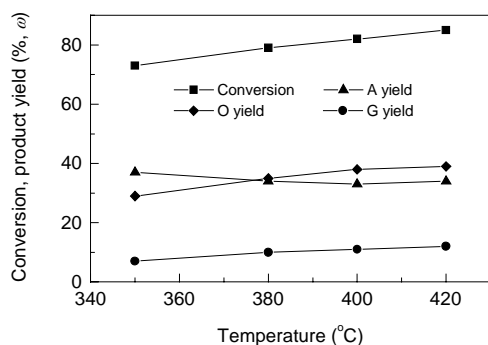


Fig.1 Effect of reaction temperature on co-liquefaction of Sample I and sawdust

Fig.2 Effect of reaction temperature on co-liquefaction of Sample II and sawdust

(Reaction conditions: sample 10 g, sawdust 10 g, tetralin 60 ml,  $t=30$  min, cold  $H_2$  pressure 3.40 MPa.)

### 3.2.3 Effect of reaction time

Co-liquefaction of Sample I or Sample II with sawdust was conducted under the operation conditions of temperature 380°C, cold hydrogen pressure 3.40 MPa, and tetralin as solvent. The recorded operation time varies within the range from zero to 60 minutes. For the case of Sample I, the conversion and oil yield, as can be seen in Fig.3, increase steadily with time while the yield of asphaltene and preasphaltene nearly remains constant owing to the fact that intermediate products from sawdust can so effectively help hydrogenation of asphaltene and preasphaltene in forming oil that the rates of formation and disappearance of asphaltene and preasphaltene keep almost equal. For the case of Sample II (Fig.4), the process underwent the same change as in the case of Sample I except for the oil yield being always lower.

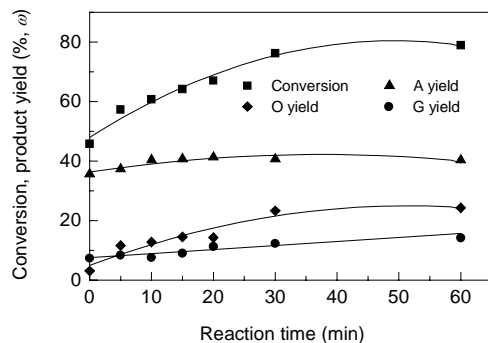
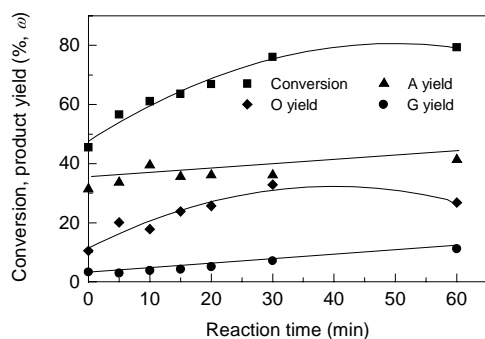


Fig.3 Effect of reaction time on co-liquefaction of Sample I and sawdust

Fig.4 Effect of reaction time on co-liquefaction of Sample II and sawdust

(Reaction conditions: sample 10 g, sawdust 10 g, tetralin 60 ml, temperature 380°C, cold  $H_2$  pressure 3.40 MPa.)

### 3.2.4 Effect of cold hydrogen pressure

Liquefaction of either coal or biomass can be considered as a consecutive process consisting of thermolysis and hydrogenation. Radical fragments formed from thermal decomposition can only be stabilized by abstraction of active hydrogen, otherwise they would polymerize, and thus liquefaction result in a low yield of oil. Hydrogenation is therefore crucial in determining product distribution. More often than not high hydrogen pressure is maintained in the liquefaction and solvents as

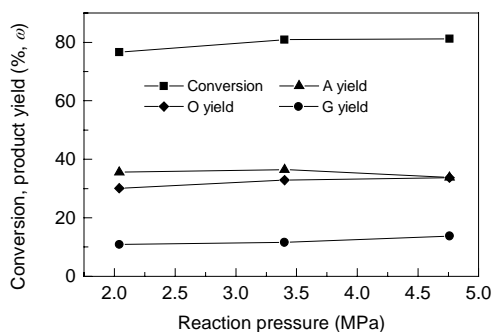


Fig.5 Effect of cold H<sub>2</sub> pressure on co-liquefaction of Sample I and sawdust (Sample 10 g, sawdust 10 g, tetralin 60 ml, T=400°C, t=30 min.)

hydrogen vehicle are used in order to improve the oil yield. Data from the tests under three different cold hydrogen pressures, 2.04, 3.40 and 4.76 MPa, are presented in Fig.5, indicating that cold hydrogen pressure can affect the process. Conversion increases by 4.66%, oil yield by 3.57% as pressure is increased from 2.04 to 4.76 MPa. Tetralin as hydrogen-donation solvent used in the tests accounts for quite moderate magnitude of increase in conversion /oil yield as compared with the increase in hydrogen pressure, which implies the important role of hydrogen vehicle.

## 4 CONCLUSIONS

Due to the fact that maceral constituent vitrinite is more readily liquefied than fusinite, variation in temperature within the operation range affects fusinite more effectively than vitrinite. Because in the first phase of liquefaction, thermolysis reactions for vitrinite have lower activation energies, the change in reaction rate is less dependent on the change in temperature. Intermediate products formed from thermolysis of sawdust help hydrogenation of asphaltene and preasphaltene in forming oil product so that oil yield rises when adequate free hydrogen can be transferred through hydrogen vehicle solvents (often together with catalysts).

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