



Co-liquefaction of rice straw and coal using different catalysts

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HIGHLIGHTS

- ▶ There exists synergistic effect in the co-liquefaction of coal and rice straw.
- ▶ The catalyst with strong acidity diminishes the synergistic effect in the co-liquefaction of coal and rice straw.
- ▶ The activity of catalyst in the co-liquefaction is different from that in individual liquefaction of coal and rice straw.

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ABSTRACT

Co-liquefactions of a Chinese Shenfu sub-bituminous coal (SFSBC) and rice straw (RS) over four different coal liquefaction catalysts were carried out and the co-liquefied product preasphaltene (PA) was characterized by elemental analysis, FTIR and gel permeation chromatograms (GPC) measurements. It was found that the four catalysts gave different catalytic activities in the liquefaction of SFSBC and RS alone. Co–Mo/Al₂O₃ and SO₄²⁻/ZrO₂ promoted the oil formation for RS liquefaction due to their solid acidic property, but FeS + S gave the highest catalytic activity for the liquefaction of SFSBC among the four catalysts used in this study. There existed a positive synergistic effect in the co-liquefaction of SFSBC and RS, and the main synergistic interaction was reflected by the promoted formation of oil and PA. The catalytic activities of the four catalysts in the co-liquefaction were quite different from their catalytic activities in the individual liquefaction of SFSBC and RS. FeS gave the lowest catalytic activity for the coal liquefaction alone among the four catalysts, but had the highest promotion to the synergistic effect in the total yield of liquefaction products in the co-liquefaction of SFSBC and RS. SO₄²⁻/ZrO₂ diminished this synergistic effect for the co-liquefaction of SFSBC and RS due to its solid acidic property. It was found that the four catalysts used have higher catalytic activity for the PA, which is from coal liquefaction and converting this part of PA into AS and oil fraction. The average molecular weights of PAs from SO₄²⁻/ZrO₂ and Co–Mo/Al₂O₃ catalysts were lower than those of PAs from FeS and FeS + S catalysts, suggesting that the catalytic hydrogenation activities of SO₄²⁻/ZrO₂ and Co–Mo/Al₂O₃ are higher than those of FeS and FeS + S catalysts.

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1. Introduction

Reduction of CO₂, one of the greenhouse effect gases, in air is growing one of hot issues in the world. Biomass such as rice straw is a cheap, abundant and the only renewable organic energy source, the liquefaction of biomass to convert into alternative transportation fuels has been paid more and more attentions [1,2]. Since reaction conditions used in the liquefaction of biomass are comparable to those applied to coal hydro-liquefaction, there have been several attempts to co-process coal and biomass [3–6]. Many studies demonstrated that there exists a positive synergistic

effect in the co-liquefaction of coal with biomass. Co-liquefaction of coal with biomass can improve the yields and quality (such as H/C ratio) of the liquid products produced from coal under milder conditions of temperature and pressure [7–11]. Stiller et al. [12] studied the liquefaction of Blind Canyon seam coal in the presence of one of four different types of agricultural and biomass wastes at 350 °C and found that the agricultural and biomass wastes interact with coal and tetralin in different ways. The incremental conversion and the asphaltene + preasphaltene yield appeared to be related to the amount of hemi-cellulose in the wastes, while the incremental oil + gas yield appeared to be related to the amount of lignin. Lalvani et al. [13] found that lignin-derived liquids when reacted with coal under mild reaction conditions (375 °C) enhanced the rate of coal depolymerization. Up to 30% enhancement

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in coal conversion was achieved using lignin-derived liquids. They explained that the enhancement in coal depolymerization rate can be related with a reaction pathway involving intermediates formed from lignin-derived liquids. Coughlin and Davoudzadeh [3] believed that thermal depolymerization of lignin at relatively low temperatures leads to the formation of resonance stabilized phenoxy radicals, which then attack the coal causing scission of aliphatic carbon–carbon bonds in the coal. We [6] have investigated the co-liquefaction of coal and rice straw (RS) and found that there exists an obvious synergistic effect between coal and RS, and this synergistic effect is the function of liquefaction conditions. It is found that coal liquefaction catalyst FeS also has high catalytic activity for the co-liquefaction of coal and sawdust [14]. Ikenaga et al. [15] found that $\text{Mo}(\text{CO})_6$ catalyst ($S/\text{Mo} = 4$) was the most effective for the respective homo-liquefaction of *Chlorella* and Yallourn coal. In the co-liquefaction, however, the oil yield slightly decreased as compared to the mean value, due to an insufficient amount of an active species at ($S/\text{Mo} = 4$). This means the catalytic behavior of coal liquefaction catalyst is different in co-liquefaction of coal and biomass from that in coal or biomass liquefaction alone.

This paper reports the co-liquefaction properties of RS and coal using different catalysts, and the catalytic activities of the four catalysts used in the co-liquefaction of coal and RS were compared with their catalytic activities in the individual liquefaction of coal and RS. The characterizations of liquefied product PA obtained from the different catalysts were discussed.

2. Experimental section

2.1. Samples and reagents

Shenfu coal (a Chinese sub-bituminous coal, SFSBC) used in this study was provided by Shenhua Group. RS was used as biomass feedstock. SFSBC and RS as received were ground to pass through 200 and 60 meshes sieve respectively, stored under nitrogen atmosphere and dried under vacuum at 80 °C overnight before use. The ultimate and proximate analyses of SFSBC and RS used are provided in Table 1. All solvents used are commercial pure chemical reagent (purity higher than 99.5%) without further purification. The purity of hydrogen used in this study is 99.9%.

2.2. Preparation of $\text{Co-Mo}/\text{Al}_2\text{O}_3$ and $\text{SO}_4^{2-}/\text{ZrO}_2$

The required amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved with distilled water, then a certain amount of Al_2O_3 was added to the solution. The solution was then heated to evaporate water, and the precipitated product was dried and calcined at 500 °C for 4 h, then was sulfided with CS_2/H_2 (CS_2 0.02 ml/min) flow at 400 °C for 2 h, and aged with N_2 flow for 7 h. The catalyst obtained was called as $\text{Co-Mo}/\text{Al}_2\text{O}_3$.

The hydroxide of Zr was obtained by hydrolyzation of ZrOCl_2 with aqueous ammonia at room temperature, and the precipitated solution was filtered, washed and dried. The hydroxide of Zr prepared was further impregnated with aqueous sulfuric acid, dried and calcined at 650 °C for 3 h. The catalyst obtained was called

Table 1
Ultimate and proximate analyses of SFSBC and RS.

Sample	Proximate analysis, wt.%				Ultimate analysis, wt.%				
	M_{ad}	A_{d}	V_{daf}	FC_{daf}	C_{daf}	H_{daf}	N_{daf}	$S_{\text{t,d}}$	O_{daf}^*
SFSBC	8.6	10.9	39.3	49.8	73.17	4.59	1.08	0.50	20.71
RS	5.6	16.2	68.3	15.5	38.40	3.71	1.35	0.22	55.35

* by difference.

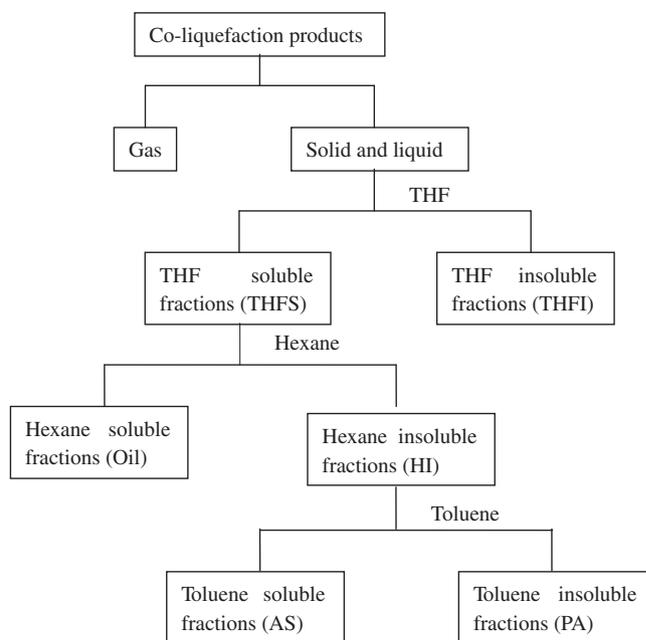


Fig. 1. Fractionation procedure of liquefied product.

as $\text{SO}_4^{2-}/\text{ZrO}_2$. A detailed description can be found elsewhere [16]. All chemicals used above were of reagent grade.

2.3. Liquefaction and product fractionation

The liquefaction experiments were carried out in a 30 ml tubing reactor shaken vertically. 1.0 g of the dried coal or sawdust or the mixture of coal and sawdust (1:1 by weight) loaded with 5% catalyst was charged into the reactor together with 2 ml of tetralin. Before the liquefaction experiment, the reactor was sealed and flushed three times with hydrogen, followed by pressuring the system to the initial pressure of 5.0 MPa with hydrogen. The reactor, agitated vertically at 120 times per min, was submerged into a eutectic salt bath, which had been heated to the desired temperature, and maintained at that temperature for desired reaction time. Then the reactor was quenched to ambient temperature in a water bath, and the overhead pressure in the reactor was released slowly. The liquefactions were conducted at 400 °C and 60 min. Four coal liquefaction catalysts were used in this study, i.e. FeS, FeS + S, $\text{SO}_4^{2-}/\text{ZrO}_2$, and $\text{Co-Mo}/\text{Al}_2\text{O}_3$.

The liquefaction mixture was separated by Soxhlet solvent extraction with tetrahydrofuran (THF), n-hexane and toluene in turn. The n-hexane insoluble but toluene soluble fraction was defined as asphaltene (AS), and the toluene insoluble but THF soluble fraction was defined as preasphaltene (PA). The fractionation procedure is shown in Fig. 1.

The total yield (TY) of liquefaction products of feedstock was defined as the THF soluble fraction + gas, which was calculated from the THF insoluble residue. Gas yield was calculated from the material weight difference before and after liquefaction with gas released. Oil yield was calculated as:

$$\text{Oil}\% = \text{TY} - \text{PA} - \text{AS} - \text{Gas}$$

The repeatability of the fractionation analyses is 1%.

2.4. FTIR and elemental analyses

FTIR were measured on a PE-Spectrum One IR spectrometer at a resolution of 4 cm^{-1} . Samples for the FTIR measurement were

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