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CO-LIQUEFACTION OF HEISHAN COAL AND RESIDUE OIL WITH BOILING TEMPERATURE >520 °C

Хейшан көмірдің сұйылтуы 1 л сыйымдылықты автоклавта, Е/К = 2, қысым 6,0 МПа, катализатор ретінде Fe_2O_3&S қолданылып жүргізілді. Еріткіш/көмір тең екі кезінде жанар майдың шығуы (68 %) максималды, еріткіш сұйылту кезінде жанар май шығуы (19 %) минималды болады. Нәтижелер көрсеткендей, еріткіш/көмір қатынасы және қысым маңызды көрсеткіштер болып табылады. Хейшан көмірінің сұйылту температурасы 400 °С-дан жоғары болуы мүмкін.

Ожижение Хейшанского угля было выполнено в автоклаве вместимостью 1 л при отношении Р/У = 2, давлении 6,0 МПа, и использовании катализатора Fe_2O_3&S. Максимальный топливный выход (68 %) был получен при соотношении Р/У = 2. Как показывают результаты, отношение Р/У и давление являются важными факторами. Температура ожижения Хейшанского угля может быть выше 400 °С.

1. Introduction

Energy sources are the need of modern civilization. Petroleum and petroleum based oils are the key sources used for power generation in the premium market i.e. as traffic fuels. Other alternative fuels are being researched recently to reduce the reliance on petroleum based oils. However, they will be in the center of the energy scene in the future. Keeping in view the heralding oil crises, there is a need to focus on carbonaceous candidate materials for conversion in to highly demanding liquid fuels. Coal is the most plentiful and versatile fuel available on earth which becomes very important both sources of energy and organic feedstock in the 21st century. There are several ways to get chemicals and synthetic fuels through coal conversing [1–5]. Coal directly liquefaction is one of the ways of coal conversion getting useful products.

2. Experimental

2.1 Materials. Basis on an iron-catalyst, Fe_2O_3 mixing with S were used in this work. The chemicals used in Experiment such as Fe_2O_3, S, *n*-hexane, toluene, THN and THF was purchased from market, and they were needn't to preparation.

Coal sample was supplied by Heishan coal mine of Shenhua Group. Residue oil was supplied from petroleum of DuShanZi in Xinjiang, China. Autoclave was made in DaLian, China. Analysis results of the samples of coal and residue oil are summarized in Table 1 and 2, respectively. Tetralin (THN) was used as liquefaction solvents.

Table 1

The proximate and ultimate analysis of coal sample, w_t %, daf

Coal sample	Proximate analysis				Ultimate analysis					H/C
	M	A_d	V_{daf}	FC[a]	C	H	O[a]	N	S	
Heishan	4,78	3,28	34,18	57,76	70,48	3,50	16,75	1,00	0,21	0,60

a: By difference.

Table 2

Properties of the residue oil after >520 °C

Wax content w_t %	Soft point °C	ductibilit 15 °C, cm	Needle degree 1/10 mm, 25 °C	Saturate w_t %	Aromatic w_t %	Gel& asphaltene, w_t %
1,87	43,5	>150	109	30,62	29,52	39,86

2.2 Liquefaction procedure. Coal liquefaction was performed in an autoclave of capacity of 1 L with electromagnetic-driven at 400 °C. The amount of sample was 30 g, solvent 60 g, and catalyst 3 wt% daf of amount of the sample (S/Fe = 2). They were charged to the autoclave together. The liquefactions were performed under 6 MPa of hydrogen pressure at reaction temperature for 60 min. The heating rate was 7~8 °C/min. The stirring speed was 300 rpm. After reaction, the reactor was cooled. The product of coal liquefaction was extracted with THF, and then separated with THF by evaporation. It was extracted with *n*-hexane, toluene and THF in sequence. The substances of *n*-hexane-soluble (HS), hexane-insoluble but toluene-soluble (HI-ACS), toluene-insoluble but THF-soluble (ACI-THFS), and THF-insoluble (THFI) were defined as oil (O), asphaltene (A), preasphaltene (PA), and residue (R), respectively. The gas yield was calculated by weight difference between initial coal and recovered product.

The oil yield was calculated by subtracting the solvent weight from the total weight of HS [6].

3. Results and discussion

3.1 Only Heishan coal liquefaction. Conditions and results of the sample hydrogenation liquefaction show in Tables 3. As shown in tables 3 the oil yield ranges 30~45 %, these data indicate that the sample decomposes lightly at 400 °C. Besides, as a catalyst Fe_2O_3 mixing with sulfur is of low activity at 400 °C, is insufficient to hydrogenate the decomposed fragments from coal and to eliminate the condensation reactions. This suggests that the sample liquefaction at temperature should excess 400 °C. Figure 1 and 2 analysis visually influence of these three factors on oil yield and liquefaction yield. If oil yield is a target, ratio of s/c is a key factor, whereas the other two factors are general factors. If liquefaction yield is a target, initial hydrogen pressure is a key factor, whereas the other two factors are general factors.

Table 3

Orthogonal designing plan of experimental conditions of the sample

№	Hydrogen Pressure P(H_2), MPa	Time, mins	S/C w: w	Oil yield, w_t%	Liquefaction yield, w_t %
1	5,0	45	1:1	36,93	53,79
2	5,0	45	2:1	37,73	57,31
3	5,0	60	1:1	31,23	51,18
4	5,0	60	2:1	44,37	53,67
5	6,0	45	2:1	43,55	66,72
6	6,0	45	1:1	29,41	57,42
7	6,0	60	2:1	44,32	63,57
8	6,0	60	1:1	37,25	65,10

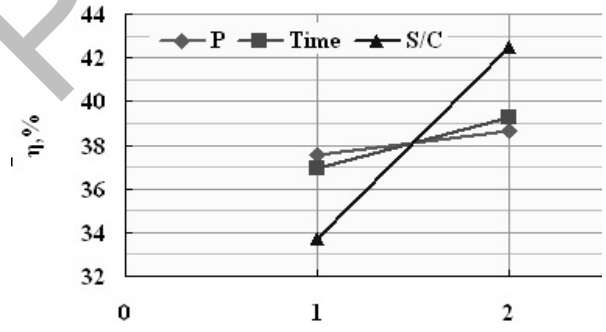

Fig. 1. Analysis Visually the relationship between three factors and oil yield

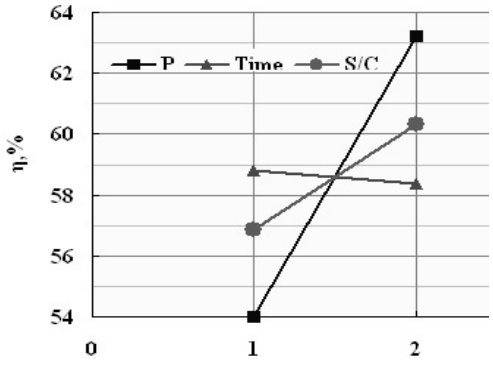

Fig. 2. Visual analysis of relation three factors with liquefaction yield

3.2 Co-Liquefaction 0f Heishan Coal and Residue Oil. Figure 3 shows to compare with yields of oil and liquefaction under different solvent conditions, that is, no solvent, tetralin, and residue oil as a solvent, respectively, at T = 673K, P_{H_2} = 6 MPa, θ = 60 min, and S/C = 2:1. As shown in figure 3 without solvent the conversion is 30.2 % and the oil yield 19.6 %, with the help of tetralin as a solvent the conversion 58,1 % and the oil yield 44,32 %, and instead of residue oil as a solvent the conversion 90,2 % and the oil yield 68.7 %. Obviously the last one is much better than first other two. It suggests that there is an significant and positive effect synergic between the coal and residue oil in the liquefaction reaction. For this point we will do further research.

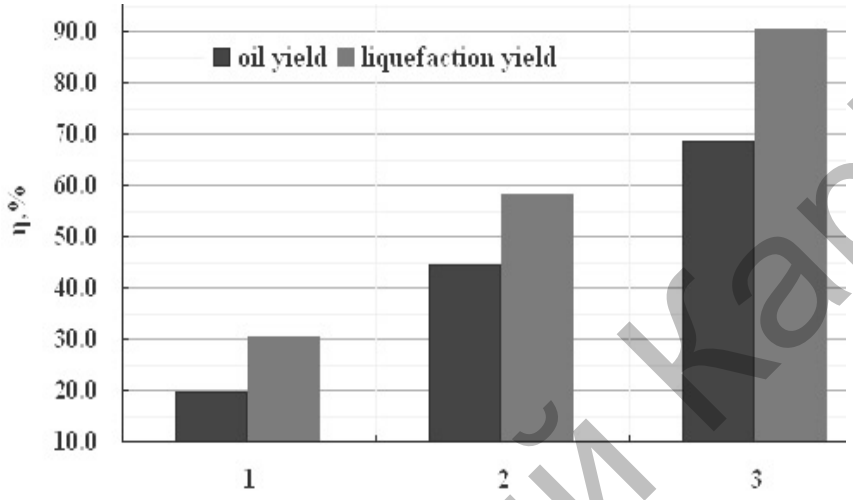

Fig. 3. Comparison yields of oil & liquefaction under at conditions: 1 — no solvent; 2 — tetralin; 3 — residue oil; T = 673 K; $P(H_2)$ = 6 MPa; θ = 60 min; S/C = 2:1

4. Conclusion

1. S/C and $P(H_2)$ are two keys factors in the coal liquefaction, and at temperature that coal decomposes maybe is above 400 °C.

2. There is an significant and positive effect synergic between the coal and residue oil in the liquefaction reaction.

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