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Article

Effect of Recycle Solvent Hydrotreatment on Oil Yield of Direct Coal Liquefaction

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Abstract: Effects of the recycle solvent hydrotreatment on oil yield of direct coal liquefaction were carried out in the 0.18 t/day direct coal liquefaction bench support unit of National Engineering Laboratory for Direct Coal Liquefaction (China). Results showed that the hydrogen-donating ability of the hydrogenated recycle solvent improved and the hydrogen consumption of solvent hydrotreatment was increased by decreasing liquid hourly space velocity (LHSV) from 1.5 to 1.0 h^{-1} and increasing reaction pressure from 13.7 to 19.0 MPa. The hydrogen-donating ability of the hydrogenated recycle solvent was enhanced, thus promoting the oil yield and coal conversion of the liquefaction reaction. The coal conversion and distillates yield of coal liquefaction were increased from 88.74% to 88.82% and from 47.41% to 49.10%, respectively, with the increase in the solvent hydrotreatment pressure from 13.7 to 19.0 MPa. The coal conversion and distillates of coal liquefaction were increased from 88.82% to 89.27% and from 49.10% to 54.49%, respectively, when the LHSV decreased from 1.5 to 1.0 h^{-1} under the solvent hydrotreatment pressure of 19.0 MPa.

Keywords: direct coal liquefaction; solvent; continuous device; hydrogen-donating; catalytic hydrotreating

1. Introduction

In direct coal liquefaction, coal is hydro-converted into liquid fuel and gas products in the presence of a solvent, gaseous hydrogen and catalyst at high temperature and pressure. Hydrogen-donor solvent plays an important role in the direct coal liquefaction process. The solvent used in direct coal liquefaction serves a number of important purposes. It provides a transport medium for the coal and facilitates heat transfer. During the reaction, it serves as an important source for the supply and delivery of hydrogen, and it also disperses the hydrogenation liquefaction products. Reviewing the development of direct coal liquefaction, the technology achieved a major breakthrough with the proposal and application of hydrogen donor solvents [1,2]. The hydrogen-donor solvent promotes the direct coal liquefaction reaction and improves the oil yield since the solvent stabilizes the coal fragment radicals by donating hydrogen. The hydrogen-donating reaction is accompanied by the dehydrogenation of partially hydrogenated aromatics such as tetrahydronaphthalene, dihydro-phenanthrene and dihydropyrene. The heavy oil fraction utilized as the hydrogen donor solvent in coal liquefaction contains a large amount of aromatics such as naphthalene, phenanthrene and pyrene. Given that these aromatics do not possess hydrogen-donating ability, they should first be hydrogenated into hydroaromatics [3–7].

In the Shenhua coal liquefaction process, the recycled hydrogen-donor solvent is a hydrogenated heavy oil product from the coal liquefaction process. The coal liquefaction oil is fed to a solvent hydrotreatment reactor, hydrogenated over a Ni–Mo catalyst in the solvent hydrotreatment reactor and then separated in the distillation section into four fractions, *i.e.*, the liquefied light naphtha with a boiling point below 145 °C, liquefied heavy naphtha with a boiling point ranging from 145 to 220 °C, the warm solvent with a boiling point ranging from 220 to 350 °C, the hot solvent with a boiling point ranging from 350 to 538 °C. All the hot solvent is used as the recycle solvent, and a part of the warm solvent is mixed with the hot solvent (and then called “recycle solvent”) and recycled back into the liquefaction reactor in the Shenhua coal liquefaction process [8].

The extent of the solvent hydrogenation directly affects the coal conversion and oil yield in the coal liquefaction process. The hydrogenated recycle solvent could enhance the hydrogen donor ability to coal. The oil yield becomes higher as the hydrogen-donating ability of the recycle solvent is higher [9–17]. Since the oil yield of coal liquefaction influences the economic benefits of the Shenhua coal liquefaction demonstration plant, the selection of the optimum solvent hydrotreatment conditions for the economically efficient production of the oils is very important for the Shenhua coal liquefaction demonstration plant. In the present paper, the effect of solvent hydrotreatment pressure and liquid hourly space velocity (LHSV) on recycle solvent hydrogen-donating ability and product yields in the Shenhua coal liquefaction process was studied in the 0.18 t/day direct coal liquefaction bench support unit (a continuous device).

2. Experimental Section

2.1. Coal

The experimental coal was sampled from the Shenhua Shangwan coal mine which provides the feedstocks for the Shenhua direct coal liquefaction demonstration plant. The coal quality and petrographic analysis data are listed in Table 1. The volatile matter of the Shangwan coal was 38.55% on a dry and ash-free (daf) coal basis. The vitrinite and inertinite content were 63.18% and 37.04% respectively. The coal contained 80.32% carbon and 4.50% hydrogen on a dry and ash-free coal basis. The atomic ratio of hydrogen to carbon was 0.67.

Table 1. Coal quality and petrographic analysis of coal sample.

w (Proximate Analysis)/%			φ (Petrographic Analysis)/%			*w* (Ultimate Analysis)/% [(1)]					$n(H)/n(C)$
M_{ad}	A_d	V_{daf}	Vitrinite	Inertinite	Exinite	C	H	S	N	O [(2)]	
8.96	13.10	38.55	63.18	37.04	0.44	80.32	4.50	0.43	1.01	13.74	0.67

Notes: M_{ad}—air-dried moisture; A_d—dry ash; V_{daf}—dry-ash-free basis volatile. (1). In dry ash-free basis; (2). By difference.

2.2. Process Flow of the 0.18 t/day Direct Coal Liquefaction Bench Support Unit (BSU)

A process flow diagram of the 0.18 t/day direct coal liquefaction bench support unit (BSU) is shown in Figure 1. The BSU consists mainly of five sections: coal slurry preparation, hydro-liquefaction reaction, vacuum distillation, solvent hydrotreatment and atmospheric distillation. The slurry, a mixture of pulverized coal, liquefaction catalyst and hydrogen-donor recycle solvent, was fed to the liquefaction reactor along with pressurized hydrogen. The effluent from the liquefaction reactors was separated into the liquefied light oil and heavy oil. The heavy oil was separated in the vacuum distillation section into the flash oil and liquefaction residue. The flash oil mixed with the liquefied light oil from coal liquefaction was used as the feedstock for solvent hydrotreatment. The mixed oil was fed into hydrogenation reactor in the solvent hydrotreatment unit. The effluent from the hydrogenation reactor was separated in the atmospheric distillation section which obtained the recycle solvent. The light naphtha fraction, heavy naphtha fraction and the remaining part of the warm solvent constitute the direct coal liquefaction product.

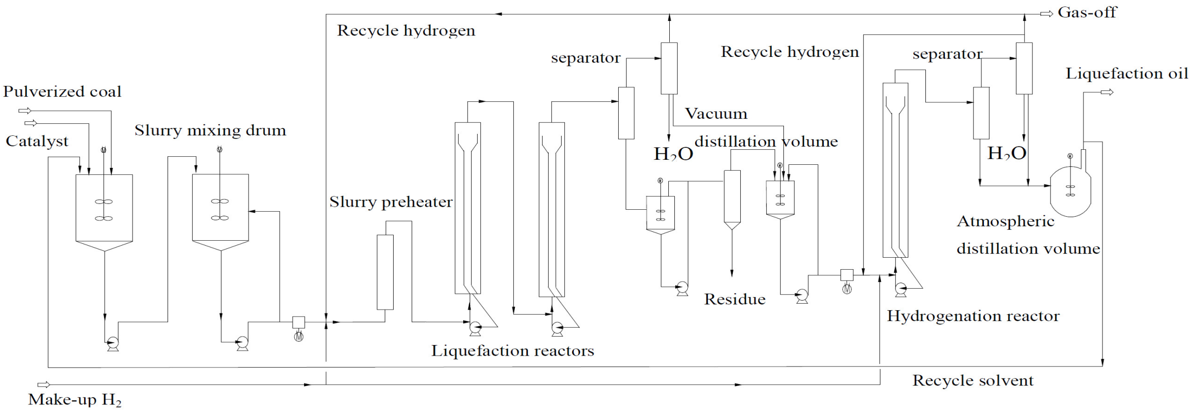

Figure 1. The process flow diagram of 0.18 t/day direct coal liquefaction bench support unit.

2.3. Experimental Procedures

The catalytic hydrotreatment of recycle solvent was carried out in the suspended bed reactor over an alumina-supported Ni–Mo catalyst co-developed by Sinopec Fushun Research Institute of Petroleum and Petrochemicals and Shenhua Group. Table 2 shows the properties of the hydrotreatment catalyst.

Shenhua coal was hydro-liquefied in two same size back-mixed reactors connected in series with a recirculation pump to provide the back mixing. A nanometer catalyst (863 catalyst) jointly developed by Shenhua Group and China Coal Research Institute was used as the liquefaction catalyst [18]. The 863 catalyst of 1.0% dry coal was prepared an addition to the feed coal slurry. Table 3 shows the composition of the coal liquefaction catalyst.

Table 2. The properties of the hydrotreating catalyst.

Item	Data
Shape (cylindrical)	-
Diameter/mm	0.9–1.1
Length/mm	3–8
Compositions/*w%*	-
MoO_3	20.6
NiO	4.6
Surface/(mm^2/g)	188.0
Pore volume/(mL/g)	0.43
Pore size/nm	33.96
Compacted bulk density/(kg/L)	0.81
Crushing strength/(daN/mm)	136

Table 3. The compositions of coal liquefaction catalyst.

Item	Composition/%						
Component	Water	Fe	$(OOH)^{3-}$	NH_4^+	SO_4^{2-}	Coal	Other
Data	5.56	5.61	3.31	0.33	0.97	84.13	0.10

Operating conditions for the tests are shown in Table 4. The tests were performed to examine the variations in the product yields of coal liquefaction as a function of the recycle solvent hydrotreatment reaction pressure and liquid hourly space velocity (LHSV).

Table 4. The operating conditions of 0.18 t/day bench support unit (BSU).

Test	Solvent Hydrotreatment			Coal Liquefaction		
	θ_1 (1)/°C	p_1 (2)/MPa	LHSV/(h^{-1})	θ_2 (3)/°C	p_2 (4)/MPa	$V(H_2)/V(Slurry)$
A	-	-	-	455.0	19.0	1000
B	375.0	13.7	1.5	455.0	19.0	1000
C	375.0	19.0	1.5	455.0	19.0	1000
D	375.0	19.0	1.0	455.0	19.0	1000

Notes: (1). Solvent hydrotreatment reaction temperature; (2). Solvent hydrotreament pressure; (3). Coal liquefaction reaction temperature; (4). Coal liquefaction pressure.

In test A, the recycle solvent was not hydrogenated, and the liquefaction oil was directly separated in the atmospheric distillation section, and then the solvent was recycled to coal slurry preparation. The coal liquefaction operating conditions were similar in the comparative experiments on the influence of recycled solvent hydrogenation degree on coal liquefaction behavior. In test B, the recycle solvent was hydrogenated at the reaction temperature of 375 °C under a hydrogen pressure of 13.7 MPa with a LHSV of 1.5 h^{-1}. In test C, the LHSV was 1.5 h^{-1} and the pressure was raised to 19.0 MPa. In test D, the pressure was 19.0 MPa and LHSV was decreased to 1.0 h^{-1}. The slurry was composed of the coal and hydrogenated recycle solvent at a coal concentration of 45 *w*%, the coal liquefaction reaction temperature was 455 °C, and total operating pressure was 19.0 MPa.

2.4. Analysis

The elemental compositions of the produced oils were measured by using CHN and S analyzers. C and H were analyzed by Thermo Flash 2000 (Thermo Fisher, Waltham, MA, USA), and N and S by multi EA-5000 (Analytik Jena AG, Jena, Germany). The percent oxygen content was determined by the subtraction of the sum of carbon, hydrogen, nitrogen, and sulfur content from 100. The naphthenic hydrogen of the hydro-aromatics contained in the solvent naphthenic hydrogen was defined as the hydrogen which shows the chemical shift ranging from 1.5 to 2.0 ppm in the ^{1}H-NMR spectrum. Proton donor quality index (PDQI) is expressed in terms of milliequivalents of β-naphthenic hydrogen of per gram of solvent and was calculated on the ^{1}H-NMR spectra and elemental composition, which expresses the hydrogen-donating ability of the solvent [19–22]. Aromaticity (f_a) was calculated based on the ^{1}H-NMR spectra and elemental composition. The hydrocarbon compositions of the recycle solvent were identified by GC-MS (Gas Chromatograph-Mass Spectrometer) analysis [23].

The residue was extracted with *n*-hexane and tetrahydrofuran. The *n*-hexane soluble fraction and *n*-hexane insoluble and the tetrahydrofuran-soluble fraction were defined as oil, asphaltene and preasphaltene (PPA), respectively. The coal liquefaction product yields and hydrogen consumption of coal liquefaction were calculated on the basis of the daf coal.

3. Results and Discussion

3.1. Effect of Solvent Hydrotreatment Pressure on the Hydrogen-Donating Ability of the Recycle Solvent

Increasing the hydrogenation reaction pressure was beneficial to hydrogenation and for enhancing the extent of solvent hydrotreatment. Table 5 shows the effect of the pressure on product distribution and hydrogen consumption in the solvent hydrotreatment. The hydrogen consumption increased from 1.18% to 1.28% with an increase in the reaction pressure from 13.7 to 19.0 MPa. The water yields changed insignificantly at 1.66% and 1.65%, respectively. The oxygen in the recycle solvent could be easily hydrogenated into the water independent of the reaction pressure. The yields of the organic gas decreased from 1.30% to 0.79%. The yields of the liquid under the reaction pressure of 19.0 MPa was more than that under 13.7 MPa, thus illustrating that the cracking reaction decreased with an increase in the solvent hydrotreatment pressure.

Table 6 shows the variation of the recycle solvent properties as a function of the hydrotreatment pressure. The nitrogen and sulfur contents in the hydrogenated recycle solvent were significantly decreased, and decreased further with the increase in the solvent hydrotreatment pressure. The density, aromaticity and hydrogen to carbon atomic ratio minimally changed little, thus indicating the recycle solvent hydrotreatment pressure did not appear to influence the properties of the hydrogenated recycle solvent, but PDQI expressing the naphthenic hydrogen content of the recycle solvent increased from

23.91 to 24.57 mg/g, thus implying an improvement in the hydrogen-donating ability of the hydrogenated recycle solvent.

Table 5. Effect of pressure on product distribution and hydrogen consumption in solvent hydrotreatment.

Test	*w* (Hydrogen)/%	*y* (Gas)/%	*y* (Water)/%	*y* (Liquid)/%
B	1.18	1.30	1.66	99.01
C	1.28	0.79	1.65	100.49

Table 6. Variation of the recycle solvent properties as a function of the hydrotreatment pressure.

Test	ρ^{20}/(g cm^{-3})	f_a	PDQI [(1)]/(mg g^{-1})	*w* (Element)/%				*n*(H)/*n*(C)
				C	H	S	N	
A	0.9745	0.50	15.00	88.93	9.96	0.0111	0.2500	1.34
B	0.9537	0.40	23.91	89.10	10.71	0.0053	0.0513	1.45
C	0.9542	0.39	24.57	88.83	10.81	0.0025	0.0257	1.46

Notes: (1). Proton donor quality index expresses the naphthenic hydrogen content of the recycle solvent.

Table 7 shows effect of solvent hydrotreatment pressure on the hydrocarbon compositions of the recycle solvent, as measured by GS-MS. The aromatic compounds were grouped into 14 components according to the type of the compounds. The number of aromatic rings ranged from 1 to 4. The hydrogen-donating ability of the solvent depends upon the molecular structure of the compounds in the solvent. Paraffins have limited hydrogen-donating ability in the direct coal liquefaction. Naphthenes and alkylbenzenes possess poor hydrogen-donating ability. Aromatic compounds containing naphthenic rings such as the naphthalenes, phenanthrenes, anthracenes and pyrenes act as hydrogen-donors, which promote the liquefaction reaction [18]. The recycle solvent hydrogenated under the pressure of 13.7 MPa showed 5.5% paraffins, 22.2% naphthenes, 71.3% aromatic compounds, and 1.0% resin. The recycle solvent hydrogenated under the pressure of 19.0 MPa was composed of 4.2% paraffins, 17.6% naphthenes, 77.0% aromatic compounds, and 1.2% resin. The non-hydrogenated recycle solvent had more aromatic compounds but less aromatic compounds with naphthenic rings, thus indicating that the hydrogen-donating ability was weak. After hydrogenation, aromatic compounds with naphthenic rings increased, which illustrated that the hydrogen-donating ability of the recycle solvent was improved. The recycle solvent hydrogenated under the pressure of 19.0 MPa contained more aromatic compounds with naphthenic rings than that hydrogenated under 13.7 MPa, which suggested that the hydrogen-donating ability of hydrogenated recycle solvent increased with the hydrotreatment pressure.

3.2. Effect of Solvent Hydrotreatment Liquid Hourly Space Velocity (LHSV) on the Hydrogen-Donating Ability of the Recycle Solvent

Decreasing the LHSV of solvent hydrotreatment promotes hydrogenation reactions and enhances the extent of solvent hydrogenation. Table 8 shows the product distribution and hydrogen consumption of solvent hydrotreatment with different LSHVs. The hydrogen consumption of solvent hydrotreatment obviously increased from 1.28% to 1.50% with the decrease in LHSV from 1.5 to 1.0 h^{-1} under the same hydrogenation pressure of 19.0 MPa. The organic gas yields increased from 0.79% to 0.94%.

The water yields slightly declined from 1.65% to 1.61%, whereas the liquid yield insignificantly changed. These results showed the further enhancement of the extent of solvent hydrogenation.

Table 7. Effect of solvent hydrotreatment pressure on hydrocarbon compositions of recycle solvent.

Component	**Composition/*w*%**		
	A	**B**	**C**
Paraffins	4.3	5.5	4.2
Naphthenes	14.3	22.2	17.6
Alkylbenzenes	2.7	7.5	5.4
Cycloalkylbenzene	17.6	20.2	22.8
Dinaphthenebenzenes	13.2	17.8	21.7
Naphthalenes	6.3	4.1	4.3
Acenaphthenes	8.0	4.6	5.8
Fluorenes	6.3	6.5	6.9
Phenanthrenes	4.4	3.2	3.4
Naphthenephenanthrenes	2.2	1.7	1.6
Pyrenes	4.5	1.9	1.7
Chrysenes	1.5	0.3	0.4
Thiophenes	4.4	2.8	3.0
Resin	9.8	1.0	1.2

Table 8. Product distribution and hydrogen consumption of solvent hydrotreatment with different liquid hourly space velocity (LHSV).

Test	***w* (Hydrogen)/%**	***y* (Gas)/%**	***y* (Water)/%**	***y* (Liquid)/%**
C	1.28	0.79	1.65	100.49
D	1.50	0.94	1.61	100.43

Table 9 shows the properties of the recycle solvent hydrogenated with different LSHVs. The aromaticity, PDQI and hydrogen to carbon atomic ratio of the hydrogenated recycle solvent all increased when the LHSV decreased from 1.5 to 1.0 h^{-1}, which illustrated the enhancement of the extent of recycle solvent hydrogenation. The nitrogen and sulfur contents in the hydrogenated recycle solvent decreased with the decrease in the LHSV. PDQI increased from 23.57 to 28.69 mg/g, thus suggesting that the naphthenic hydrogen contents in the hydrogenated solvent increased. These results indicated the further improvement of the hydrogen-donating ability of the recycle solvent.

Table 9. The properties of the recycle solvent hydrogenated with the different LSHV.

Test	**ρ^{20}/(g cm^{-3})**	**f_a**	**PDQI/(mg g^{-1})**	***w* (Element)/%**				**n(H)/n(C)**
				C	**H**	**S**	**N**	
C	0.9542	0.39	24.57	88.83	10.81	0.0025	0.0257	1.46
D	0.9556	0.35	28.69	88.73	10.91	0.0017	0.0132	1.48

Table 10 shows the hydrocarbon compositions of the solvent hydrogenated with different LSHVs. The condensed aromatic compounds containing naphthenic rings exhibited higher hydrogen donating ability than the compounds containing only aromatic rings or naphthenic rings. The recycle solvent hydrogenated under the pressure of 19.0 MPa and with the LHSV of 1.0 h^{-1} contained 3.1% paraffins, 15.9% naphthenes, 78.6% aromatic compounds, and 2.4% resin. The total saturated hydrocarbons content decreased when the LHSV decreased from 1.5 to 1.0 h^{-1}. The monoaromatics increased and especially the content of monoaromatics with naphthenic rings reached 47.2%. The diaromatics content changed minimally, whereas the polyaromatics decreased. These results showed the repeated enhancement of the hydrogen-donating ability of the recycle solvent.

Table 10. The hydrocarbon compositions of the solvent hydrogenated with different LSHVs.

Component	**Composition/*w*%**	
	C	**D**
Paraffins	4.2	3.1
Naphthenes	17.6	15.9
alkylbenzenes	5.4	6.2
Cycloalkylbenzene	22.8	24.3
Dinaphthenebenzenes	21.7	22.9
Naphthalenes	4.3	6.3
Acenaphthenes	5.8	5.1
Fluorenes	6.9	5.6
Phenanthrenes	3.4	2.7
Naphthenephenanthrenes	1.6	0.8
Pyrenes	1.7	1.8
Chrysenes	0.4	0.1
Thiophenes	3.0	2.8
Resin	1.2	2.4

3.3. Effect of the Hydrogen-Donating Ability of the Recycle Solvent on Coal Liquefaction Behavior

The effect of the solvent hydrotreatment pressure and LHSV on the coal liquefaction was investigated in the 0.18 t/day BSU. The hydrogen-donating ability of the recycle solvent was enhanced by increasing the pressure and decreasing the LHSV in the solvent hydrotreatment. Table 11 shows the effect of the hydrogen-donating ability of the recycle solvent on coal liquefaction behavior. When the recycle solvent was hydrogenated, the coal conversion and the oil yield in the coal liquefaction obviously improved. When the solvent hydrotreating pressure was increased from 13.7 to 19.0 MPa with the LHSV of 1.5 h^{-1}, the coal conversion and the oil yield both improved slightly. The coal conversion increased from 88.74% to 88.82%. The distillates yield, which contained the coal liquefaction light oil and flash oil separated in the vacuum distillation, improved from 47.41% to 49.10%. The extracted oil yield, which contained distillates and the *n*-hexane soluble fraction extracted from liquefaction residue, increased from 55.14% to 57.42%. The yields of gas, water and PPA were basically constant. The hydrogen consumption in the coal liquefaction was increased a little from 4.87 to 4.95%. This shows that the hydrogen-donating ability of hydrogenated recycle solvent resulted in the promotion of liquefaction reaction for the production of oils and the coal conversion.

When the LHSV in the solvent hydrotreatment decreased from 1.5 to 1.0 h^{-1} under the pressure of 19.0 MPa, the coal conversion increased from 88.82% to 89.27%. The yield of the distillates and extracted oil both significantly increased from 49.10% to 54.49% and from 57.42% to 61.53%. The gas yield decreased from 12.90% to 12.59%. The water yield slightly changed. The PPA decreased from 10.75% to 9.15%, and the hydrogen consumption in the coal liquefaction increased from 4.95% to 5.24%.

According to direct coal liquefaction reaction mechanisms, the free radicals from coal thermal dissociation can be stabilized by the addition of a hydrogen atom or combine to form stable, high molecular mass products, leading ultimately to char or coke formation. Solvents with the strong hydrogen-donating ability can donate hydrogen and stabilize the free radicals, The PPA is hydrogenated and cracked into oil further and the heavy oil which could not be distilled is cracked into small molecule compounds under the hydrogen. The conversion of PPA into oil is the controlling step of the whole direct coal liquefaction reaction process. A decrease in the PPA and the heavy oil which could not be distilled which were cracked, results in the increase in the distillates and extracted oil. It is clear that the hydrogen-donating ability of the recycle solvent is the key factor to determine the oil yield, and the oil yield becomes higher when the hydrogen-donating ability of the solvent is higher.

Table 11. Effect of the hydrogen-donating ability of the recycle solvent on the coal liquefaction.

Test	x **(Coal)/%, daf**	w **(1)/%, daf**					w **(3)/%, daf**
		Distillates	**Extracted oil (2)**	**Gas**	**Water**	**PPA**	
A	88.51	44.78	53.65	13.91	10.41	12.84	5.45
B	88.74	47.41	55.14	13.53	10.46	10.56	4.87
C	88.82	49.10	57.42	12.90	10.99	10.75	4.95
D	89.27	54.49	61.53	12.59	9.95	9.15	5.24

Notes: (1). Product distribution; (2). Containing the oil in the residue; (3). Hydrogen consumption.

4. Conclusions

On the basis of the data on the properties of the solvents and coal liquefaction experiments in the 0.18 t/day direct coal liquefaction bench support unit, the influence of the solvent hydrotreatment pressure and LHSV solvent hydrogen-donating ability on the Shenhua coal liquefaction process behavior can be summarized as follows:

(1) Increasing the reaction pressure from 13.7 to 19.0 MPa and decreasing the LHSV from 1.5 to 1.0 h^{-1} in the solvent hydrotreatment, which both enhanced the extent of solvent hydrogenation and the hydrogen consumption, was beneficial for the hydrogenation reaction. The nitrogen and sulfur contents of the hydrogenated recycle solvent were decreased. Meanwhile, aromatics were partially hydrogenated. The hydroaromatics contents and PDQI of the hydrogenated recycle solvent were increased whereby the hydrogen donating ability of the recycle solvent was improved.

(2) The coal conversion and oil yield were significantly improved with the hydrogenated recycle solvent. As the solvent hydrogenation conditions became more severe, coal conversion and oil yield were gradually enhanced. The coal conversion and distillates yield reached 89.27% and 54.49%, respectively, when the recycle solvent was hydrogenated under a hydrogen pressure of 19.0 MPa with a LHSV of 1.0 h^{-1}. This is due to the fact that the hydrogen donating ability of the recycle solvent increased constantly under severe hydrogenation conditions, which in turn promoted the liquefaction reaction for the production of oils and the coal conversion.

(3) The hydrogen-donating ability of recycle solvent was the key factor to determine the oil yield, and the oil yield becomes higher as the hydrogen-donating ability of the solvent becomes higher.

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Author Contributions

All authors conceived and designed the research. Gao performed the experiments and processed the experiments data. Zhang and Li guided the he experiments. Gao wrote the paper. Zhang and Li reviewed and edited the manuscript. All authors read and approved the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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