NEW DEVELOPMENTS IN DEEP HYDROCONVERSION OF HEAVY OIL RESIDUES WITH DISPERSED CATALAYSTS: THE EFFICIENCY OF HYDROGEN DONORS ADDITION IN HYDROCRACKING OF LIAOHE VACUUM RESIDUE WITH DISPERSED CATALYSTS.

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Introduction

Among other future challenges, refineries must cope with heavy feed stocks of lower quality, i.e, with higher viscosity, Conradson Carbon, heteroatom content and metal content. Furthermore, to satisfy market demand for light petroleum cuts, improved treatment of the "bottom of the barrel" is needed. To achieve deep conversion of heavy residues into distillates, it is necessary to develop new hydrocracking processes because of theirs applicability. Among these hydrocracking processes, "slurry-bed" hydrocracking seems to be a promising process to converse poor-quality petroleum residues into distillates. During reaction time, inhibition of excessive coke yield is critical in high conversion of heavy poor-quality feed stocks in order to keep the reaction units smoothly operating. According to literature and patents[1], the dispersed catalysts in reaction system could be an important inhibitor of coking.

It is well known that hydrogen donor solvents have been employed into coal hydroliquefaction [2-4] and some processes of oil residues such as hydrogen-donor visbreaking (HDV)[5-6] . However, they have never been used with the combination of dispersed catalysts in heavy petroleum residue upgrading. Hydrogen donors exhibit hydrogen-donating properties and inhibit coke formation [5-9]. Thus the donor could reduce coke yield, which was added into hydroconversion system of heavy oil residue with dispersed catalysts.

Experimental

The heavy oil chosen was Liaohe vacuum residue. Its main characteristics are C%,86.9%,H%,11.0%,N%,1.08%,S%,0.43%,Ni,123ppm,V,2.9ppm,Fe,38ppm,Ca,96,density,0.9976,CCR,19.0.

The oil-soluble metal compounds tested were molybdenum-dithiocarboxylate (MoDTC), FeNaphthenate (Fenaph), NiNaphthelate (Ninaph), CoNaphthelate (Conaph). Runs were conducted batch-wise in an 100cm^3 stainless steel autoclave pressured with H_2(7.0 or 5.0Mpa cold) . About 30g feed and the catalyst precursor and Tetralin(5 or 10wt% to feed) were introduced. Element sulfur(0.1000g)was added into the autoclave to keep the catalysts totally sulfurized. The run temperature were attained in 40 mins by heating stove and efficient stirring ensured dispersion of the oil-soluble metal compounds. After run completion, gases were vented off and a solid fraction was seperated from the liquid effluent by centrifugation in toluene. The fractions(150-350^{0}C ,350-450^{0}C) were distillated after toluene was recovered. Naphthalene and Tetralin in 150-350^{0}C fraction were analyzed for donating yield by GC. Conversion of the feed into distillates were calculated by the difference between the weight of the residue feed and of coke and reacted resid.

Results

The inhibition for coking of the catalysts is known for us and take an important role in achieving deep conversion of residues[1].The four oil-soluble catalysts tested were all effective for hydrocracking of Liaohe VR . The catalytic activities of base metals were in order of :Mo>Co>Ni>Fe(see Table 1). RN of Mo was 3.51 and of Fe was 8.63 .This means that MoDTC provide the smallest coke yield in the four metals tested when achieving the same conversion. After combined with 10%wt tetralin, the coking yields were considerably decreased at the same conversion, and more VGO yields were achieved comparing with non-addition of tetralin, and hydrocracking conversion could hardly be affected . In this case, the order of inhibiting coke still was Mo>Co>Ni>Fe, all of the RN became smaller, but Mo combined with tetralin was more outstanding for reducing coke yields and RN .(see Fig.1—4 and Table 1). Only Mo combined with tetralin could remain higher activity for inhibiting coking during the most reaction time.

Literature and patents[1] show that most of the "slurry-bed" hydrocracking processes employed disposable catalysts under high hydrogen pressure (up to 20Mpa). It is necessary to reduce the amounts of used catalysts in order to decrease the cost of catalysts at the same time the reactors maintain smooth operation. However , excessively coking would generate if insufficient coke inhibitors such as active catalysts existed in the reaction system. But combined with small amounts of tetralin, little amounts of catalysts play the same part in decreasing coke yields. Table 2 show that 60ppm Mo combined with 10%wt tetralin could decrease coke yields from 3.54% to 0.98%wt, on the other hand ,500ppm Mo alone give 1.45%wt. 30ppm Mo combined with 10%wt tetralin provide smaller coke yields than 100ppm Mo alone .

To take advantage of hydrogen donor, it is necessary to combine with reasonable amount of dispersed catalysts. The disposed catalysts will be saved and the expense of operation will be decreased.

Conclusion

It was found that hydrogen donor has efficient inhibition of the coke production. Dispersed catalysts combined with hydrogen donors would be a way to upgrade heavy petroleum residues. More active catalysts with the addition of donors could yield less coke. The amounts of employed catalysts could be reduced and high hydroconversion would be achieved at non-excessive coke formation by way of this method.

Literature cited

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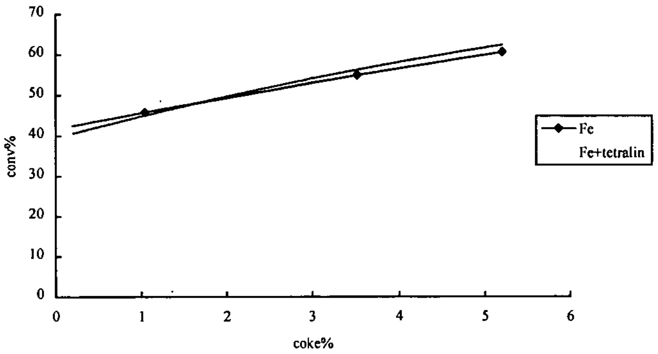

Figure 1.Comparison between Fenaph and Fenaph+Tetralin residue hydrocracking.

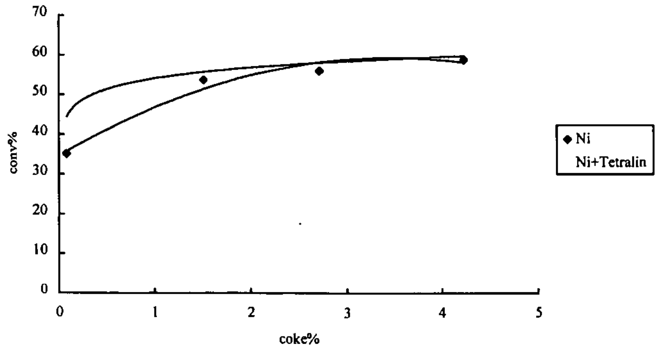

Figure 2. Comparison between Ninaph and Ninaph+Tetralin residue hydrocracking.

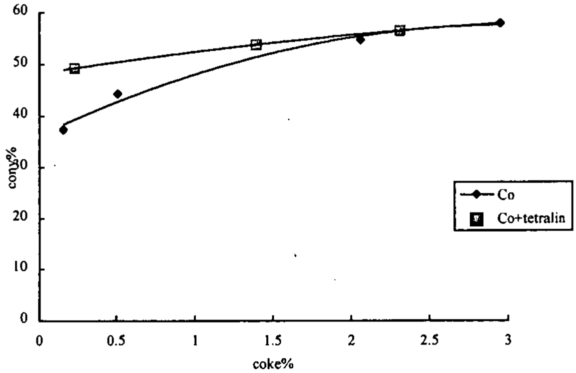

Figure3.Comparison between Conaph and Conaph+Tetralin residue hydrocracking.

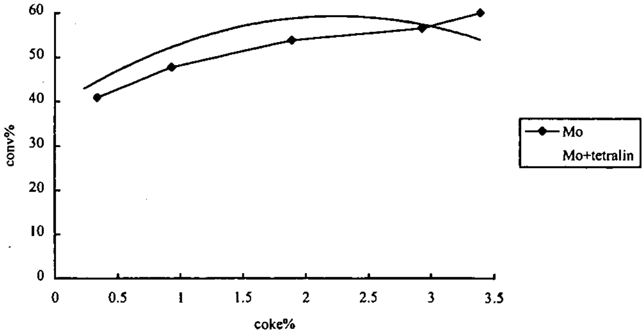

Figure 4 Comparison between MoDTC and MoDTC+Tetralin residue hydrocracking.
(all experimental conditions of the four figures are 430°C,7.00Mpa,200ppmmetal ,10.00%Tetralin)

Table 1 Hydroconversion of LHVR in the presence of Mo,Co,Ni,Fe and 10.00wt%Tetralin
(at 430oC,60 mins ,200ppm base metal and 7.0Mpa,cold)

	product yields ,wt%				conv. of resids. wt%	&RN
	<350°C	350~450°C	>450°C	coke		
MoDTC	31.12	22.71	47.37	1.89	53.83	3.51
	25.14	27.29	47.57	0.71	52.43	1.35
Ninaph	34.13	21.50	44.37	2.72	55.63	4.89
	30.90	23.90	45.20	1.89	54.80	3.45
Conaph	30.96	24.00	45.04	2.06	54.96	3.75
	27.65	26.15	46.20	1.39	53.80	2.58
Fenaph	37.78	22.60	39.62	5.21	60.38	8.63
	33.98	24.61	41.42	4.06	58.58	6.93

footnotes:1. &RN =(coke %/conv.of resids %*100) 2. is 200ppm metal+10.00wt%tetralin.

Table 2 Hydroconversion of LHVR in the presence of MoDTC and Tetralin
(at 430°C , 60mins and 7.0Mpa H_2 at cold)

	0%tetralin		5.00%tetralin		10.00%tetralin	
MoDTC	coke wt%	conv wt%	coke wt%	conv wt%	coke wt%	conv wt%
30ppm	4.45	58.80	2.95	56.30	2.25	54.76
60ppm	3.54	56.90	2.71	55.79	0.98	53.81
100ppm	2.89	54.65	1.11	53.49	0.74	52.98
200ppm	1.89	53.83	0.94	52.85	0.71	52.43
500ppm	1.45	50.90	1.05	49.54	0.75	48.42.

footnote: conv% =(feed-coke-reacted resids)%wt