

IRON BASED CATALYSTS FOR COAL/WASTE OIL PROCESSING

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ABSTRACT

Iron based catalysts are being used in our laboratory to process coal with waste oil. Almost 1.2 billion gallons of waste oil are generated in the United States each year, posing an environmental hazard due to metal bearing compounds and high sulfur content. Waste oil is primarily paraffinic and is a poor hydrogen solvent, but contains surfactants which could help in better dispersion of the coal particles and the catalyst during liquefaction. The undissolved coal can act as a trap for the metals removed from the waste oil without significantly altering the metal content of the coal. The initial results - coal conversion over 70% and oil yield greater than 48% indicate that coprocessing coal with waste oil is beneficial. The results are preliminary and responses in coal conversion and selectivity due to different ratios of waste oil and conventional hydrogen solvents are being evaluated. The effect of various parameters such as temperature, pressure and the amount of catalyst on coal conversion and selectivity during coprocessing is being evaluated.

INTRODUCTION

The coprocessing of coal with used oil has the potential to improve the economics of coal liquefaction. Almost 1.2 billion gallons of waste oil are generated in the United States each year, posing an environmental hazard due to metal bearing compounds and high sulfur content. The used oil must be re-refined and hydrotreated before use as a fuel or as a lube base stock. The reactions during the hydrotreatment of used oil include hydrodesulfurization (HDS), hydrodemetallation (HDM) and hydrodeoxygenation (HDO). The undissolved coal during coprocessing could act as a trap for the metals removed from the oil and the sulfur present in the oil could serve to produce the sulfided catalyst needed for liquefaction. The overall objective of this work is to evaluate the beneficial effects of coprocessing coal with waste oil using iron based catalysts.

The use of unsupported dispersed catalysts for conversion of coal to liquids via direct coal liquefaction is believed to be a very effective method to overcome the limitations of supported metal catalysts [1]. The restricted access to the reaction surface of the supported metal catalysts such as CoMo/Al₂O₃, used in direct coal liquefaction prevents them from influencing the reactions of coal and high molecular weight coal derived products. In addition, supported metal catalysts suffer from rapid deactivation. Unsupported dispersed catalysts provide efficient contact of coal/solvent slurries with the catalyst surface [1]. The effective dispersion of the catalysts can be achieved by different methods such as using water soluble [2] or oil soluble precursors [3] and by using finely divided powders [4]. These techniques allow formation of the active inorganic phase under reaction conditions. The addition of finely divided solid precursors with high specific surface area is considered a very effective way to achieve good dispersion and improved overall coal conversion and selectivity to oil production in direct coal liquefaction [4,5].

Iron based catalysts have the potential to be used as effective dispersed catalysts and have been employed recently for direct coal liquefaction. Iron based catalysts are cheap, readily available and disposable. Sulfated iron oxide was found to be an effective catalyst for liquefaction with 86 wt% conversion and 50 wt% selectivity for oils [6]. The addition of elemental sulfur to the catalyst was found to further increase the conversion and selectivity. It was postulated that the sulfate group inhibits agglomeration of the metal oxides and subsequently increases the surface area and catalyst dispersion [6]. Oil soluble iron carbonyls have been used in direct coal liquefaction and in coprocessing with heavy oil in a number of studies [3,7-10]. The iron carbonyls are distributed throughout the coal/solvent mixture and decompose upon heating to form very small catalyst particles active for liquefaction of coal. The addition of sulfur in either elemental form or as an organic sulfur compound favored the formation of pyrrhotite whereas the less active iron oxide (Fe_2O_3) was formed in its absence [8]. The iron pentacarbonyl precursor was converted to pyrrhotite at the reaction conditions with time. The use of 0.5 wt% iron as iron pentacarbonyl increased the coal conversion from 39% to 82% [3]. Hematite (Fe_2O_3) was found to be a very good sulfur scavenger during coal desulfurization [11]. The iron oxide reacts with all the hydrogen sulfide released to form pyrrhotites and prevents any reaction of hydrogen sulfide with the organic constituents of the process solvent. The formation of pyrrhotites as the major phase has also been reported when iron oxide was presulfided in a mixture of hydrogen and hydrogen sulfide under reaction conditions [12].

Waste oil is primarily paraffinic and is a poor hydrogen donor solvent. It does, however, contain surfactants which could be advantageous to liquefaction. The additives found in the waste oil such as detergent/dispersant additives, oxidation inhibitors, etc., are organic sulfur compounds [13]. These additives could help effectively disperse the coal and the catalyst precursors throughout the coal/oil slurry during coprocessing. In addition, these additives can serve as sulfur sources to convert the catalyst precursors to the more active form. The unconverted coal could act as a trap for the metals removed from the oil. This has been the case during coprocessing of coal with a heavy oil where metallic impurities in the oil were found to deposit on the coal residue or pitch [14]. The demetallation of used oil during hydrotreatment was found to be primarily due to the process of physical deposition on the catalyst bed [15].

EXPERIMENTAL

The co-processing reactions in the tubing bomb were carried out using DECS 6 coal, waste oil (1% sulfur, 0.45% ash), tetralin as a solvent (in some cases), and superfine iron oxide (Fe_2O_3) as a catalyst precursor. The coal was crushed and separated to obtain a particle size of less than 16 mesh. The liquid and solid reactants were then charged in the desired proportions into a tubing bomb reactor. High pressure hydrogen was added through a fine metering valve and capped with a Swagelok fitting. The bomb was leak tested by submerging it in water. The bomb was then attached to a variable-speed motor via an extension arm. The bomb was then lowered into a fluidized sand bath to maintain the reaction temperature and was shaken vertically. At the end of the desired reaction time, the motor was stopped and the tubing bomb was removed from it. The reaction was then quenched using water at room temperature. The liquid and solid reactant mixture was filtered under vacuum to separate the solid and liquid components. The liquid portion was saved for sulfur and ash analysis. The bomb and the solids collected

in the first filter were then washed with hexane to obtain the hexane-soluble fraction. The solids remaining after hexane washing were allowed to dry before weighing. The solids were then washed with tetrahydrofuran (THF) to obtain the THF solubles. This solid was also allowed to dry before being weighed. The liquid obtained from the first filter was then tested for sulfur content using a LECO sulfur determinator (SC-32) and ash content was determined using a SYBROM Thermolyte furnace.

RESULTS AND DISCUSSION

The coal conversion during coprocessing with waste oil was defined as

Conversion = $100 * (1-X)$ where,

$$X = \frac{W_R - W_C - W_{ash}}{W_{ash\ free\ coal}}$$

W_R weight of residue remaining after THF wash,

W_C weight of catalyst (it was assumed that all the iron oxide was converted to FeS)

W_{ash} weight of ash in the coal

The results from coprocessing experiments are given in Table 1 (using superfine iron oxide) & Table 2 (using Fisher grade iron oxide).

The reduction in sulfur and ash are for the oil obtained after the first filter on the basis of initial analysis of waste oil. The conversion and the oil yield are very high (88% and 69% respectively) even when only coal and oil are used. The conversion increased when either tetralin or catalyst precursor (iron oxide) was added to the reaction mixture. The oil yield remained nearly same. However, both the conversion and oil yield decreased when both tetralin and iron oxide were added. The reason for this behavior is not very clear at this time and additional experiments are being conducted for confirmation. The amount of iron oxide used in these runs was the stoichiometric amount (2.5 wt% based on the oil) needed to remove all the sulfur in the waste oil. However, when the iron oxide was used in excess (1.5 times the stoichiometric amount), and the amount of tetralin was increased, the conversion and the oil yield increased as expected (89% and 48% respectively).

The reduction in the sulfur content was greater when tetralin was present in the system. This is probably due to the increased availability of hydrogen in the liquid phase when tetralin is present, leading to increased removal of sulfur by forming hydrogen sulfide. The reduction in the ash content was greater than 70% in most of the runs. The ash reduction is believed to be primarily due to the deposition of the metals on unreacted coal and residue [14,15].

CONCLUSIONS

Coprocessing coal with waste materials such as waste oil which have expensive disposal costs offers several advantages. Unsupported dispersed catalyst precursors (iron oxide) were used in an initial study to coprocess waste oil with coal. The conversion of the coal

and the selectivity for the oil was in excess of 70% for most of the runs. The conversion and the selectivity were higher even when the catalyst precursor was not used. The sulfur and the ash content in the oil were reduced substantially during coprocessing. A detailed study is underway at present to evaluate the effect of various parameters such as different ratios of oil to hydrogen donor solvents, temperature, pressure, catalyst loading, etc., on the coal conversion and selectivity.

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Coproducting Coal with Waste Oil						
Table 1.						
CATALYST (wt%)	TETRALIN* (wt%)	TIME (min)	CONVERSION* (%)	OIL YIELD® (wt%)	SULFUR REDUCTION (%)	ASH REDUCTION (%)
6 grams of oil, 0.6 grams of DECS 6 coal						
-	-	60	87.84	69.27	35.80	84.10
2.50	-	60	96.13	65.64	28.85	89.06
-	20	60	93.03	70.39	38.30	72.22
2.50	20	60	71.48	36.27	40.40	-
3.75	60	30	88.93	47.68	54.90	90.67
9 grams of oil, 0.9 grams of DECS 6 coal						
-	-	30	88.96	80.37	27.00	80.02
-	-	60	71.50	71.77	27.20	73.27
-	-	90	88.87	87.12	-	38.22
2.5	20	60	91.88	35.31	40.80	75.82

* catalyst precursor: superfine iron oxide (Fe_2O_3).

+ based on amount of oil.

tetrahydrofuran (THF) soluble MAF basis.

@ oil yield on basis of coal converted.

Reaction conditions: 400 °C, 1200 psig (at room temperature).

Table 2.
COPROCESSING COAL WITH WASTE OIL

WASTE OIL (gms)	TETRALIN (gms)	TEMPERATURE (°C)	OIL ANALYSIS*		OIL YIELD** (MAF)
			SULFUR REDUCTION (%)	ASH REDUCTION (%)	
20	-	410	30	80	55%
20	-	430	40	65	55%
10.14	10.53	430	40	85	75%

Reaction Conditions: Blind Canyon (DECS 6) coal: 2 gms; Fe₂O₃ (Fisher grade): 0.75gms.
1000 psig hydrogen pressure (at room temperature)

* Initial Analysis: Sulfur 1.01%; Ash content: 0.43%

** based on initial coal charge