

IRON CATALYSTS IN COAL HYDROGENATION

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ABSTRACT

Hydrogenation of a set of low and high rank coals was studied using iron containing species as catalyst. Three catalytic precursors were used: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (IS), Fe_2O_3 (RM) and $\text{Fe}(\text{CO})_5$ (IP). The addition of catalyst increased the conversion in important extent when low rank coals were hydrogenated and in a more moderate way with the bituminous coals under an initial hydrogen pressure of 10 MPa and in absence of solvent, dry hydrogenation. When CS_2 was added to high sulphur content coals only slight increase of oils formation was observed. However, significative higher conversions to asphaltenes and oils were reached when the coal sulphur content was around 1%. It seems to be more important the amount of total sulphur than its organic or inorganic nature.

INTRODUCTION

Coal hydrogenation processes consists in coal transformation into progressively lighter products in order to obtain oil. In general, the product distribution of processes such as hydroliquefaction and hydroypyrolysis, shows a mixture of low-molecular weight oils, asphaltenes and preasphaltenes, as well as the insoluble residue. The hydrogenation has been widely used, not only for its interest in hydrocarbon production, but also as an strategy of degradative reaction applied to coal in order to study the coal structure.

Both approaches to coal, the practical and the theoretical one, seem to be nowadays not yet resolved, regardless the great research effort that is been done, in many senses, process development, variables optimization and catalyst selection.

Iron containing compounds have been widely studied as hydrogenation catalysts, due to their relatively low cost, hydrogenation activity and iron decarboxilation potential. Several ways of iron addition to the coal can be used. Each one presents advantages and drawbacks. The iron precursors dispersion onto the coal surface is now generally considered to have a beneficial effects, that increases the amount of active catalyst surface area available at the same loads. This dispersion requires the previous dissolution of the precursors and several of the compounds of interest as liquefaction catalysts, such pyrite, iron oxide, are insoluble in common solvents. Other solid precursors have to be added by physical mixing. The organometallic species are usually added with the hydrogenation solvent; when the working procedure is dry, liquid species as $\text{Fe}(\text{CO})_5$ can be just added to the coal previously to the introduction into the reactor. In all the cases, the active form of the iron catalyst is considered to be the iron sulphide.

The aim of this work is to study the effect of the hydrogenation temperature and catalysts on the product distribution and characteristics, when the hydrogenation is carried out in absence of solvent, keeping constants the initial hydrogen pressure and the hydrogenation time.

EXPERIMENTAL

The work reported is part of a broader investigation (1) of dry catalytic hydrogenation of a set of 25 coals from different mining areas around the world. For this paper, the results

obtained with 9 of these coals, 6 from Spain (Ref. S9, S13, S16, S18, S20 and B23), one from USA (Illinois No 6, Ref. B19), one from Germany (Zollverein, Ref. B22) and one from UK (Bagworth, Ref. B25). The low-rank coals are from Mequinenza (S9), Andorra-Ariño (S13, S16 and S18) and Portalrubio (S20) and were selected as a function of their nature(2). The analysis of the coals are compiled in Table 1.

Catalyst Precursors

Three iron containing precursors with iron in different oxidation stages were used: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Red Mud (36.5% Fe_2O_3) and $\text{Fe}(\text{CO})_5$. The first one was converted "in situ" into iron sulphide by H_2S bubbling for 30 min through the alkaline aqueous solution. Then was dispersed on coal using coal as catalytic support. The two others precursors were added to coal before hydrogenation by direct physical mixing (RM) or by embedding ($\text{Fe}(\text{CO})_5$). The catalyst loading was equivalent to 5% wt iron of dmmf coal.

Hydrogenation Procedure

The hydrogenation was carried out in small reactors type tubing bomb (160cc capacity) loaded with about 10 g of daf coal and catalyst, pressurized with H_2 to 10 MPa and heated in a fluidized sand bath for 30 min at 300, 350, 400, 425, 450 and 500°C. When the coal sulphur content was low, CS_2 was added.

The products work-up was according to Fig 1. The gas were analyzed by GC, the oils by elemental analysis, FTIR, TLC-FID and simulated distillation by GC. The THF-insolubles by CP-MAS 13C nmr and FTIR

RESULTS AND DISCUSSION

As the numerical data on conversions and derived product distributions of each coal would enlarge this paper, tables 2 and 3 show the results obtained with coals Ref. S13 and B25 as representative models. However, comments on the other hydrogenated coals will be done along this paper since each coal has its own characteristics.

The selected coals, apart from low and high rank coals can be classified as high and low sulphur content coals. The percentages are calculated on "as received" basis. While the low rank coals have %S ranging from 8.6% to 5.7%, the bituminous coals show a total sulphur content around 1%, with the exception to B19 with 3.9% of total sulphur. That is the reason why to very few experiments has been added CS_2 , see Table 2, when S13 coal has been hydrogenated. Coals S13, S16, and S20 have about the same organic sulphur contents (4%), while S18 has more pyritic sulphur (3.80%) and S9 has much more organic sulphur (7.78%). Not one of these coals need CS_2 addition to reach high conversions in iron catalytic hydrogenation and when CS_2 was added not significative variations were detected on conversion percentages nor THF-solubles; only a very slight increase in oils formation percentages were obtained.

Keeping constants the hydrogenation time and the starting hydrogen pressure, in general, the higher the temperature, the higher the conversions, the THF-solubles and the oils percentages.

The very high conversions (95% dmmf for the S9 coal) reached with these low-rank high-sulphur content coals seem to show that it does not matter the origin of the sulphur, organic or inorganic, the real point seems to be the total amount of sulphur present in order to reach the H_2S pressure to convert the iron (whatever be its original oxidation degree) from the catalytic precursor into the iron sulphide salt which is the active form (3). On the other side the SEM analysis shows that if the H_2S pressure is sufficient at the end of the processes most of the iron is in the sulphide form. The optical microscopy shows the superficial, not yet the nucleous, transformation of the pyrite nodules from the inherent mineral matter into pyrrhotite on the THF-insolubles from non-catalyzed test at 300 °C. This

transformation is complete at 350 °C.

The presence of iron catalyst increased coal conversion from 47% to 75% (IS), 60% (RM) and 59% (IP) at 350 °C and from 76% to 89% (IS), 95% (RM) and 91% (IC) at 400°C when S9 coal was hydrogenated. With the bituminous coals the difference between non-catalytic and catalytic processes was not so pronounced, but significant enlargement was reached when CS₂ was added.

For the B22, B23, and B25, Table 3, at the lowest temperature studied, the addition of CS₂ is not determinant because at this temperature there are not yet thermic nor catalytic cracking with these high rank coals, but at the medium temperatures studied, 350°C and 400°C, the CS₂ addition influences helping to stabilize the radicals from both thermic and catalytic cracking. The bituminous coal with an intermediate total sulphur content (B19) follows the same trends but the effect of CS₂ addition is significant in a minor extent.

The nature of the oils, analyzed by TLC-FID, show to be mainly aromatic and polar, with percentages in saturate compounds always minor to 3% . On polar percentages, the nature of the iron precursor is not relevant but the increase of the process temperature means a reduction of polars to the corresponding aromatic compounds.

The curves of simulated distillation, from the oils by GC analysis, show that there are not conversion into light fractions with low-molecular weight, the gas oil fraction is very scarce, always lower than 2% and the rest of the components are heavy oils.

The transformation of coal into liquids has been followed by solid state nmr spectroscopy of the THF insolubles, Tables 5 and 6. Due to the magnetic properties of this analytical technic and to the iron catalysts used, in some of the spectra was not easy the chemical shift assignation, so only the aliphatic (0-100 ppm) and aromatic (100-190 ppm) carbons have been assigned. These troubles were deeper when RM than when FeSO₄ was used. In order to do not lose rigor, the simplification was done in all the cases. It can be deduced a gradual diminution in the length of the alkylic chains and with increasing hydrogenation temperature, an increasing aromaticity slightly higher when red mud is the catalytic precursor. The FTIR (Fig. 2), confirms the disappearance of aliphatic chains, the decrease in oxygen groups and the aromaticity increase.

Summarizing, at the conditions studied, it can be concluded: a) The importance of the total amount of sulphur in order to reach the suitable H₂S pressure, being not significant the organic or inorganic nature of the parent sulphur. b) The CS₂ addition does not influence the yields from high-sulphur content coals, but increases conversions and THF-solubles, mainly asphaltene formation, when about 1 % is the inherent sulphur content of coals. c) The iron of the catalytic precursor is converted into pyrrhotite in a higher extension when it comes from IS than from RM.

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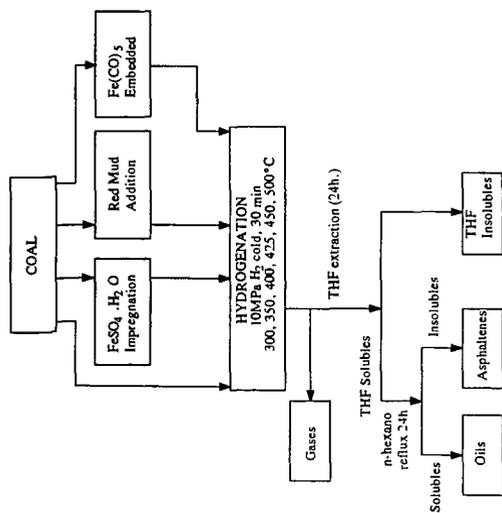


Figure 1. Diagram of the process.

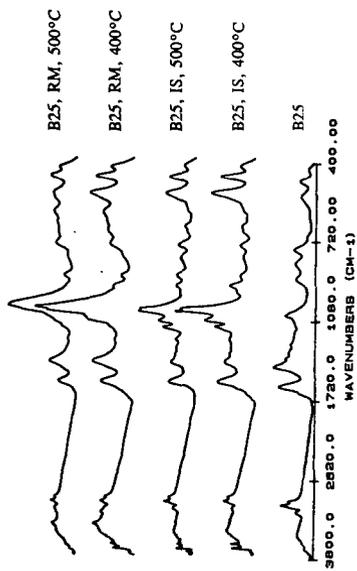


Figure 2. FT-IR spectra of THF-insolubles of B25 coal hydrogenation and raw coal.

Table 2. Conversions and product yields (daf) from S13 coal (10MPa H2 cold and 30 min).

Cat.	Tem. °C	% CS2	% Conv	%THF sol.	O/A	%Gas formation		
						COx	C1-C4	SH2
-	350	-	32.4	23.4	0.1	69	4	27
-	350	YES	37.7	26.9	0.2	71	5	25
-	450	-	80.5	56.3	0.4	46	18	37
IS	300	-	15.8	9.1	0.4	98	0	2
IS	350	-	82.0	69.6	0.1	78	6	16
IS	400	-	78.7	54.2	0.5	54	16	29
IS	425	-	80.2	48.9	0.7			
IS	450	-	84.8	51.2	1.1	45	41	14
RM	300	-	12.1	8.6	0.5	100	0	0
RM	350	-	33.1	23.2	0.3	86	8	5
RM	350	YES	35.6	23.9	0.4	79	8	14
RM	400	-	87.9	60.9	0.4	57	20	23
RM	425	-	84.4	53.5	0.4			
RM	450	-	64.7	30.9	0.8	50	39	11
IP	350	-	34.4	26.0	0.2	83	3	14
IP	350	YES	61.3	40.2	0.2	85	4	11
IP	400	-	75.8	50.9	0.2	69	20	12

Table 3. Conversion and product yields (daf) from B25 coal (10MPa H2 cold and 30 min).

Cat.	Tem. °C	% CS2	% Con.	%THF sol.	O/A	%Gas formation		
						COx	C1-C4	SH2
-	350	-	14.2	8.3	0.8	77	7	14
-	400	-	39.2	32.5	0.4	51	36	13
-	450	-	40.4	22.5	1.1	41	54	5
IS	300	-	11.3	9.2	0.3	97	0	3
IS	350	-	21.3	17.3	0.2	96	0	4
IS	400	-	70.7	55.9	0.4	56	37	7
IS	425	-	79.1	58.1	0.5	43	50	7
IS	450	-	71.7	45.8	1.3	38	59	3
IS	500	-	74.1	32.0	1.3	23	73	4
RM	300	-	5.5	9.3	0.5	100	0	0
RM	300	YES	3.6	10.5	0.3	49	1	50
RM	350	-	14.7	13.3	0.3	92	8	0
RM	350	YES	19.2	19.7	0.3	48	10	43
RM	400	-	43.9	37.9	0.4	67	31	1
RM	400	YES	69.5	60.5	0.3	45	20	34
RM	425	-	73.9	55.6	0.4	50	49	1
RM	425	YES	75.1	59.8	0.6	29	28	43
RM	450	YES	70.2	44.2	0.8	24	36	40
RM	500	YES	64.6	32.8	1.4	22	72	6
IP	350	-	12.6	12.4	0.6	98	2	0
IP	350	YES	9.2	17.1	0.4	90	3	7
IP	400	YES	71.9	61.3	0.4	60	14	25
IP	450	YES	73.7	35.8	0.8	55	33	12

Table 1. Analysis of the parent coals.

Coal Ref.	Proximate analysis (%)				C. fix.	Ultimate analysis (%)			Macerales (%vol)				
	C/H	Moist.	Ash	%MM		Volat.	C	H	N	S	tot	Vitrin.	Exin.
S 9	0.68	11.03	21.35	27.65	36.48	31.14	44.15	5.39	0.39	8.65	90.9	0.4	8.7
S 13	0.74	17.04	11.29	19.48	29.53	42.14	48.34	5.47	0.29	6.00	71.8	3.1	25.1
S 16	0.81	12.94	11.10	18.81	29.51	46.15	49.24	5.07	0.49	6.38	74.7	1.6	23.7
S 18	0.92	12.04	15.11	24.20	29.07	43.78	49.10	4.99	0.35	6.33	75.4	1.0	23.6
S 20	1.07	9.30	38.60	58.06	22.15	29.95	38.18	2.95	0.39	5.71	62.7	1.3	36.0
B 19	1.14	3.30	13.34	17.20	31.59	31.78	64.17	4.67	1.21	3.92	89.1	1.7	9.2
B 22	1.33	1.10	12.07	12.08	25.88	60.95	72.33	4.52	1.49	0.98	67.0	9.0	19.0
B 23	1.58	0.80	8.30	11.43	16.95	74.27	82.23	4.35	1.67	1.20	92.9	0.0	7.1
B 25	1.24	13.70	7.60	11.39	34.10	44.60	62.49	4.19	1.06	1.06	72.0	5.0	23.0

Table 4. Oils nature as a function of the hydrogenation variables (10 MPa H₂, cold and 30 min).

Coal	Variables	Cat.	Tem.(°C)	Oil Composition (%)		
				Sat.	Arom.	Polars
S13	-	350	1.9	56.0	42.1	
S13	-	400	1.5	68.4	30.1	
S13	IS	300	2.0	39.5	58.5	
S13	IS	350	2.0	56.0	42.0	
S13	IS	400	1.4	67.6	31.3	
S13	RM	300	2.0	39.5	58.5	
S13	RM	350	2.2	49.4	48.5	
S13	RM	400	1.4	60.7	37.9	
B25	-	350	2.4	46.9	52.0	
B25	-	400	5.9	60.9	36.4	
B25	IS	300	2.1	45.4	52.5	
B25	IS	350	2.2	48.5	49.3	
B25	IS	400	2.5	57.3	40.3	
B25	IS	425	2.5	57.3	40.3	
B25	RM	300	2.8	29.0	68.3	
B25	RM	350	2.4	46.0	51.7	
B25	RM	400	2.6	58.4	38.3	
B25	RM	450	1.7	55.5	42.8	

Table 5. Aromaticity and functional groups by CP-MAS Cl₃ nmr of S13 THF-insolubles.

Chemical Shift(ppm)	Raw		Blank runs		S13 IS			S13 RM		
	Coal	300°C	350°C	300°C	300°C	350°C	400°C	300°C	350°C	400°C
0 - 100	33.0	25.5	21.4	53.0	26.4	22.0	68.0	35.5	24.6	
100 - 190	67.0	74.8	81.1	139.0	135.0	131.0	135.5	155.0	157.0	
Aromaticity	0.66	0.71	0.78	0.71	0.82	0.85	0.67	0.78	0.84	

Table 6. Aromaticity and functional groups by CP-MAS Cl₃ nmr of B25 THF-insolubles.

Chemical Shift(ppm)	Raw		B25 IS			B25 RM		
	Coal	300°C	400°C	500°C	300°C	350°C	400°C	500°C
0 - 100	33.0	35.8	15.5	7.3	34.8	26.8	11.8	12.2
100 - 190	72.0	62.9	84.3	92.7	65.2	73.2	88.2	87.8
Aromaticity	0.66	0.64	0.84	0.92	0.65	0.73	0.88	0.96

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