

CATALYTIC COAL LIQUEFACTION USING SYNTHESIS GAS

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INTRODUCTION

Recent energy shortages and environmental problems underline the great importance of desulfurizing coal to produce low-sulfur fuels. Efforts are in progress in many organizations to develop catalytic hydrogenation processes for producing liquid fuel from coal. Unfortunately, most hydrogenation processes require enormous amounts of expensive hydrogen and some significant breakthrough is needed before an economical process can be realized. A major effort must be made to reduce the high cost of hydrogen. One approach is to utilize low cost synthesis gas as the process gas to achieve equal or better results.

There have been some attempts to use carbon monoxide or carbon monoxide-containing gas for liquefying lignite (1), hydrotreating hydrocarbonaceous liquids (2), and desulfurizing heavy liquid hydrocarbon (3). The process of liquefying lignite with carbon monoxide and water does not work well on bituminous coals, and does not desulfurize coal very effectively. The hydrotreating and desulfurization of heavy liquid hydrocarbons appears to proceed well with carbon monoxide or carbon monoxide-containing gas in the presence of steam and an active metal catalyst. We have also reported that organic wastes have been hydrotreated with synthesis gas and cobalt molybdate-sodium carbonate catalyst and converted to oil (4).

The present work deals with an effort to develop an economical process for coal liquefaction-hydrodesulfurization using low cost synthesis gas in the presence of cobalt molybdate and sodium carbonate catalysts. While hydrogenation and desulfurization are catalyzed by cobalt molybdate, the water-gas shift reaction and reduction of coal by carbon monoxide are catalyzed by sodium carbonate. Hydrogen consumed is replenished partly during the hydrogenation by the following catalytic reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$. As a result, an effective hydrogenation is accomplished by eliminating large amounts of the oxygen in coal as carbon dioxide. It is noteworthy that the conversion of the oxygen in coal to water is one of the main hydrogen-consuming reactions in coal liquefaction.

EXPERIMENTAL

The liquefaction of coal was studied in a 500-ml magnetically-stirred stainless steel autoclave. Illinois No. 6 high-volatile bituminous coal and Kentucky Homestead high-volatile bituminous coal were used (table 1). A high boiling alkyl-naphthalene-based oil (boiling above 235°C) and oil products from the Kentucky bituminous coal -- SYNTHOIL (5) -- were used as vehicles. The catalyst was a silica promoted cobalt molybdate supported on alumina (Harshaw CoMo 0402T)* used either with or without sodium carbonate. The catalyst pellets were crushed before use. For most of these experiments, hydrogen and synthesis gas with H_2 :CO ratios of 1:1 and 2:1 were used at initial pressures of 1500 to 1800 psi. Operating pressures ranged from 2400 to 3400 psi at reaction temperatures of 370° to 450°C and the

*Reference to a product name is made to facilitate understanding and does not imply endorsement by the U. S. Bureau of Mines.

reaction was maintained for 5 to 60 minutes at the reaction temperature. After the experiment, rapid internal water cooling of the autoclave to ambient temperature was achieved. Total products were filtered at ambient or warmer temperatures to obtain liquid oils. Filter cakes containing residue and water were extracted by benzene. The water was removed by azeotropic distillation, and the remaining oil was recovered by removing the benzene with a rotary vacuum evaporator. Gaseous products were analyzed by mass spectrometry. Data on conversion, oil yield, hydrogen consumption, and carbon dioxide formation, etc., are given as weight-percent based on moisture- and ash-free (maf) coal.

TABLE 1. Analyses of coal, percent

Coal	C	H	N	S	O	Ash	Moisture	VM
Illinois No. 6								
bituminous								
As used	64.8	5.2	1.3	3.46	14.0	11.2	6.0	38.3
maf	78.3	5.5	1.6	4.18	10.5			46.3
Kentucky Homestead								
bituminous								
As used	58.8	4.9	1.2	5.16	14.4	15.5	7.1	35.7
maf	75.9	5.4	1.6	6.67	10.5			46.1

RESULTS AND DISCUSSION

Using $\text{H}_2:\text{CO}$ Synthesis Gas. In initial experiments, high sulfur bituminous coal was liquefied and desulfurized by hydrotreating with synthesis gas (approximately equal parts of hydrogen and carbon monoxide) in the presence of $\text{CoMo-Na}_2\text{CO}_3$ catalyst and an alkylnaphthalene vehicle oil ($S = 0.42\%$). Using Illinois No. 6 hvbb coal ($S = 4.18 \text{ maf } \%$) with 25 to 35% added moisture at a coal:vehicle ratio of 1:2.3, 3400 to 4000 psi operating pressures, and 450°C reaction temperature, averages of 91% conversion and 58% oil yield were obtained. The oil product contained an average of 0.38% sulfur.

Further experiments were carried out using a benzene soluble oil product ($S = 0.5\%$, kinematic viscosity = 2515 centistokes at 60°C) from Kentucky bituminous coal as the starting vehicle at an initial pressure of 1500 psi and 430°C reaction temperature. Various amounts of water (0 to 15 parts per 100 parts of coal plus vehicle) were added in different runs to determine the effect of moisture content of coal. In each succeeding run, the oil product recovered from the preceding run was used as vehicle. The results are shown in Table 2 and compared with that obtained from hydrogen runs which also used the same coal oil as the starting vehicle. Average data of three successive hydrogen runs are given in the table. The degree of hydrodesulfurization appears to be satisfactory at 430°C for both synthesis gas and hydrogen runs, but there is a significant decrease in hydrogen consumption and an increase in carbon dioxide formation in the synthesis gas runs. In the synthesis gas runs, the addition of water improved desulfurization and caused less hydrogen but more carbon monoxide to be consumed. The increase of moisture content has no significant effect, however, on coal conversion nor oil yield.

TABLE 2. Effect of water on hydrotreating of coal
 Illinois bituminous coal:recycle oil = 1:2.3
 (1,500 psi initial pressure, 430°C, 30 min)

	Synthesis gas (1H ₂ :1CO)				H ₂
		CoMo ¹	CoMo ¹ + Na ₂ CO ₃ ¹		CoMo ¹
Catalyst					
Water added, parts/100 parts coal + vehicle	0	5	10	15	0
Operating pressure, psi	2,500	3,000	3,400	3,800	2,400
Conversion, %	88	92	92	94	91
Oil yield, %	55	62	58	57	62
H ₂ consumption, %	4.6	3.0	1.5	1.2	6.0
CO consumption, %	50	65	90	94	-
CO ₂ formation, %	46	85	108	113	1
CH ₄ formation, %	5.4	4.5	4.9	5.0	3.0
S in oil product, %	.41	.37	.29	.29	.21
Kinematic viscosity of oil product, cs at 60°C	109	88	57	36	57

¹ Two parts per hundred parts coal plus vehicle.

Data are given in weight percent of maf coal.

Comparisons between the use of synthesis gas and hydrogen were also made at various temperatures. Data shown in Table 3 are taken from the last of three successive runs at each temperature. With decreasing temperature, using either gas, conversion decreases, oil yield increases, sulfur content in oil increases, and kinematic viscosity of oil product increases. In the hydrogen runs, hydrogen consumption is far greater and oil viscosity is more susceptible to temperature change. It is noteworthy that the product from reaction with synthesis gas and CoMo-Na₂CO₃ catalyst at 400°C is quite fluid at room temperature even after many recycle runs. On the other hand, the product from reaction with hydrogen and CoMo catalyst at the same temperature is quite viscous and the viscosity increases with each recycle run. The possibility of obtaining fluid and easily filtered oil products at lower temperatures in the synthesis gas-CoMo-Na₂CO₃ system than in the hydrogen-CoMo system may prove to be advantageous. The amount of low molecular weight hydrocarbon gases produced was small but increased with temperature.

Additional comparative data were obtained using Kentucky bituminous coal. The starting vehicle was pretreated with synthesis gas or hydrogen at specific conditions (see Table 4) prior to its use for subsequent coal liquefaction experiments. Again, at 400°C, the product from the reaction with synthesis gas, steam, and CoMo-Na₂CO₃ catalyst was least viscous.

Using 2H₂:1CO Synthesis Gas. The effect of reaction time was studied using 2H₂:1CO synthesis gas. Experiments were conducted at an operating pressure of about 3,000 psi and reaction temperatures of 425° to 450°C. Kentucky bituminous coal and a SYNTHOLL product (S = 0.17%, kinematic viscosity = 18 cs at 60°C) were used at a coal:vehicle ratio of 1:2.3. In the synthesis gas runs, 5 parts of water, 2 parts of CoMo catalyst, and 1 part of Na₂CO₃ catalyst per hundred parts of coal plus vehicle were added. Coal conversions of 85 to 92% and oil yields of 40 to 60% were obtained with 5 to 60 minutes reaction times in both synthesis gas and hydrogen runs (see Figure 1). No significant difference was found between

the two systems. The oil yield was nearly constant for all reaction times at 425°C, but decreased significantly after 15 minutes reaction time at 450°C. At high temperatures, long residence time causes further cracking of the product oil to form low molecular weight hydrocarbons. These observations suggest that the optimum liquefaction temperature is in the vicinity of 425° to 450°C and that a short residence time is practical.

TABLE 3. Hydrotreating of coal at various temperatures
(Illinois bituminous coal:recycle oil = 1:2.3, 1500 psi initial pressure, 30 min.)

Catalyst	Synthesis gas (1:1)			H ₂	
	CoMo ¹ + Na ₂ CO ₃ ¹ 10			CoMo ¹ 0	
Water added, parts/100 parts coal + vehicle					
Temperature, °C	430	400	370	430	400
Operating pressure, psi	3,400	3,400	3,400	2,400	2,400
Conversion, %	95	92	87	91	86
Oil yield, %	58	61	65	62	63
H ₂ consumption, %	1.5	0.2	-0.5	6	4
CO consumption, %	90	85	85	-	-
CO ₂ formation, %	108	101	103	1	1
CH ₄ formation, %	4.9	3.0	2.1	3.0	1.2
Oil analysis, %					
C	87.7	86.7		89.0	87.4
H	7.6	8.0		7.7	8.1
N	1.4	1.5		1.1	1.2
S	0.29	0.36	0.39	0.21	0.34
O	3.0	3.4		2.0	3.0
Kinematic viscosity, cs at 60°C	57	148	1,480	57	2,967

¹ Two parts per hundred parts coal + vehicle.

Data are given in weight percent of maf coal.

Figure 2 shows that the sulfur content and the viscosity of the oil product both decrease with increasing temperature and reaction time, but at the expense of the oil yield at 450°C. Regardless of the reaction temperature, the oil properties correlated well with the net amount of H₂ consumed in the respective system. As shown in Figure 3, the viscosity and the sulfur content of the oil product decrease with the amount of H₂ consumed. It is evident that the amount of H₂ required to attain the same level of oil quality is considerably less in the synthesis gas system than in the hydrogen system (see solid lines). When the amount of H₂ formed (equal to the amount of CO₂ formed) by the water-gas shift reaction is taken into account (dashed lines in Figure 3), the consumption of hydrogen is still less with synthesis gas. This finding suggests that carbon monoxide could be beneficial to the coal liquefaction reaction. Carbon monoxide could act to depolymerize coal, to stabilize the decomposition radicals, to prevent repolymerization, and to deoxygenate coal.

The Consumption of Reactant Gases. The consumption of gases in the coal liquefaction reaction varies with reaction variables. In particular, the consumption of synthesis gas depends a great deal on the H₂/CO ratio, the amount of water, and the presence or absence of Na₂CO₃ catalyst because of the concurrent water-gas shift reaction taking place. Table 5 shows some analyses of off-gas obtained at various conditions. The operating pressure was 3,000 psi and the amount of water added was 5 parts per hundred parts coal plus vehicle in each of the synthesis gas runs. The gas consumptions are also shown.

TABLE 4. Hydrotreating of Kentucky bituminous coal at 400°C
(1,500 psi initial pressure, 30 minutes)

	Synthesis gas (1:1)		H ₂
	CoMo ¹	CoMo ¹ + Na ₂ CO ₃ ¹	CoMo ¹
Catalyst			
H ₂ O added, parts/100 parts coal and vehicle	0	10	0
Operating pressure, psi	2,400	3,100	2,500
<u>Hydrotreating vehicle</u>			
S in oil product, %	0.31	0.30	0.29
Kinematic viscosity at 60°C	411	171	1,079
<u>Hydrotreating coal</u> (coal:vehicle = 1:2.3)			
S in oil product, %	0.30	0.30	0.33
Kinematic viscosity, cs at 60°C	348	231	2,330
Conversion, %	83	88	85
Oil yield, %	55	60	63
H ₂ consumption, %	3.7	1.0	4.0
CO consumption, %	41	80	-
CO ₂ formation, %	27	91	0.6
CH ₄ formation, %	3.0	2.8	1.2

¹ Two parts of pulverized material per 100 parts coal and vehicle.

Data are given in weight percent of maf coal.

The significant formation of carbon dioxide indicates that, in the catalytic hydro-treating of coal using synthesis gas, large amounts of the oxygen in coal are removed as carbon dioxide. The H₂/CO ratio of the off-gas leaving the reactor is greater than the feed gas. The total gas consumption and the CO/H₂ consumption ratio (scf of CO consumed divided by scf of H₂ consumed) are greater with 1H₂:1CO synthesis gas than with 2H₂:1CO synthesis gas. The H₂ consumption is greatest when hydrogen is used.

Liquefaction Process Using Synthesis Gas. It appears that synthesis gas with CoMo-Na₂CO₃ catalyst can be used in a coal liquefaction process. Sodium carbonate can be dissolved in the added water and mixed with coal. As an illustration, a simplified schematic flow diagram of a conceptual coal liquefaction process using synthesis gas is shown in Figure 4. The gas stream flow in scfh (on 100 lb/hr coal feed basis) and volume percent are shown in Table 6. The calculation was based on the data at 450°C and 15 minutes (see Table 5) requiring a CO/H₂ consumption ratio of 1.33. Thus a supply of 0.75 H₂:1CO synthesis gas is introduced to the recycle gas (H₂/CO = 2.9) to make up the feed gas with the composition of 2H₂:1CO. Using an oil yield of 3 barrels per ton of coal, the synthesis gas (0.75 H₂:1CO) consumption is calculated to be 4,000 scf per barrel of oil. In comparison, based on the similar data for the hydrogen run at 450°C and 15 minutes (Table 5), the hydrogen consumption would be 4,700 scf per barrel of oil when the feed gas is hydrogen.

TABLE 5. Analyses of off-gases and gas balance
(Coal:vehicle = 1:2.3, operating pressure = 3,000 psi)

Feed gas	Synthesis gas (H ₂ :CO = 1:1)		Synthesis gas (H ₂ :CO = 2:1)		H ₂	
	Temperature, °C	430	450	425	450	425
Time, min.	30	30	30	15	30	15
Water added, parts/100 parts coal + vehicle	5	5	5	5		
Catalyst	CoMo ¹ + Na ₂ CO ₃ ¹		CoMo ¹ + Na ₂ CO ₃ ²		CoMo ¹	
Off-gas analysis, %						
H ₂	39.8	41.8	62.7	64.5	96.1	96.0
CH ₄	3.5	4.2	1.8	2.5	1.2	1.7
C ₂ H ₆	1.4	1.0	0.7	1.0	0.6	0.7
CO	29.3	31.5	23.4	22.5		
CO ₂	24.4	20.5	10.1	9.5	0.2	0.1
H ₂ /CO ratio	1.35	1.33	2.68	2.86		
Gas balance, scf/lb maf coal						
Input	33	33	34	34	40	40
Output	27.8	27.0	31.2	30.3	32.5	32.2
H ₂ consumed	5.5	6.3	3.1	3.3	8.8	9.0
CO consumed	8.7	10.3	4.2	4.4		
CO ₂ formed	7.2	8.2	3.2	2.8		
CO/H ₂ consumption ratio	1.58	1.64	1.35	1.33		

¹ Two parts per hundred parts coal plus vehicle.

² One part per hundred parts coal plus vehicle.

TABLE 6. Gas stream flows
(Basis: 100 lb/hr coal feed)

Stream	Total flow, scfh	Gas composition, %				
		H ₂	CH ₄	C ₂ H ₆	CO	CO ₂
1	2,700	67			33	
2	2,400	64.5	2.5	1.0	22.5	9.5
3	2,090	74			26	
4	610	43			57	

The use of synthesis gas as the feed gas may be applied to SYNTHOIL, H-Coal, CONSOL, and other catalytic hydrogenation processes. The advantages are obvious: (1) the high cost of hydrogen production is saved, and the thermal efficiency increased; (2) the synthesis gas usage is lower, and the supply can be obtained at less cost than hydrogen from the gasification of the char produced in the process; and (3) the off-gas, after scrubbing out carbon dioxide and hydrogen sulfide, is a low-Btu gas. With the H₂/CO ratio of about 3, it is suitable for use in methane production or methanol synthesis. If one recycles the gas only a small bleed stream is necessary to keep CH₄ level down. The bleed gas could be burned for process heat.

CONCLUSIONS

High sulfur bituminous coal can be liquefied and desulfurized by hydrotreating with synthesis gas at 3,000 psi and 425° to 450°C in the presence of cobalt molybdate-sodium carbonate catalyst, steam, and recycle oil. The sulfur content and the viscosity of the oil product both decrease with the amount of hydrogen consumed whether synthesis gas or hydrogen is used as the reactant gas, but less total hydrogen is required for the same oil product quality when synthesis gas is used. The synthesis gas consumption is low -- 4,000 scf per barrel of liquid fuel product. The cost of hydrogen production is saved, and the off-gas can be optionally burned as a low-Btu gas or utilized for methane production or methanol synthesis.

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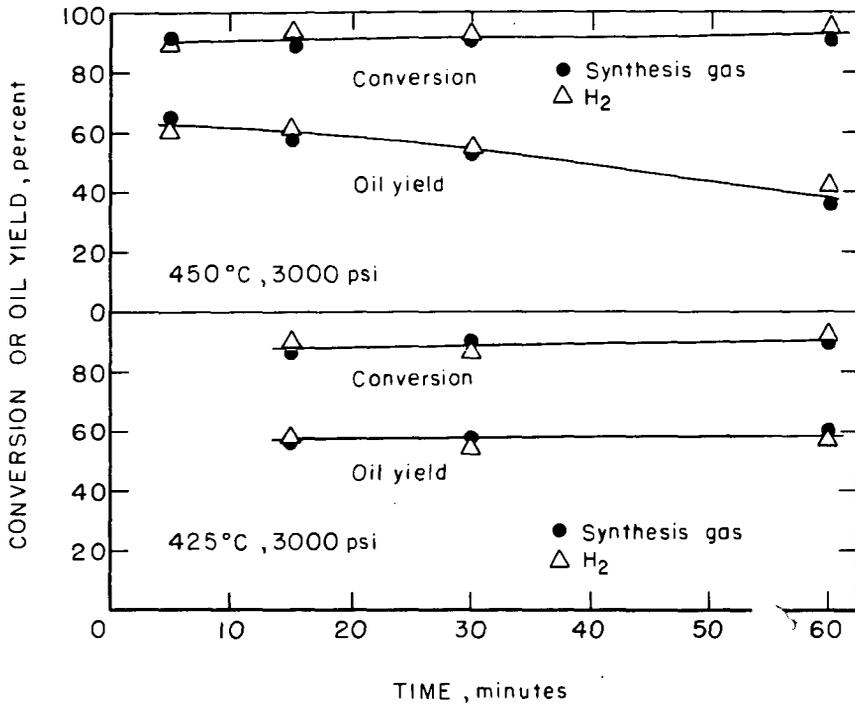


Figure 1 - Conversion and oil yield vs reaction time.

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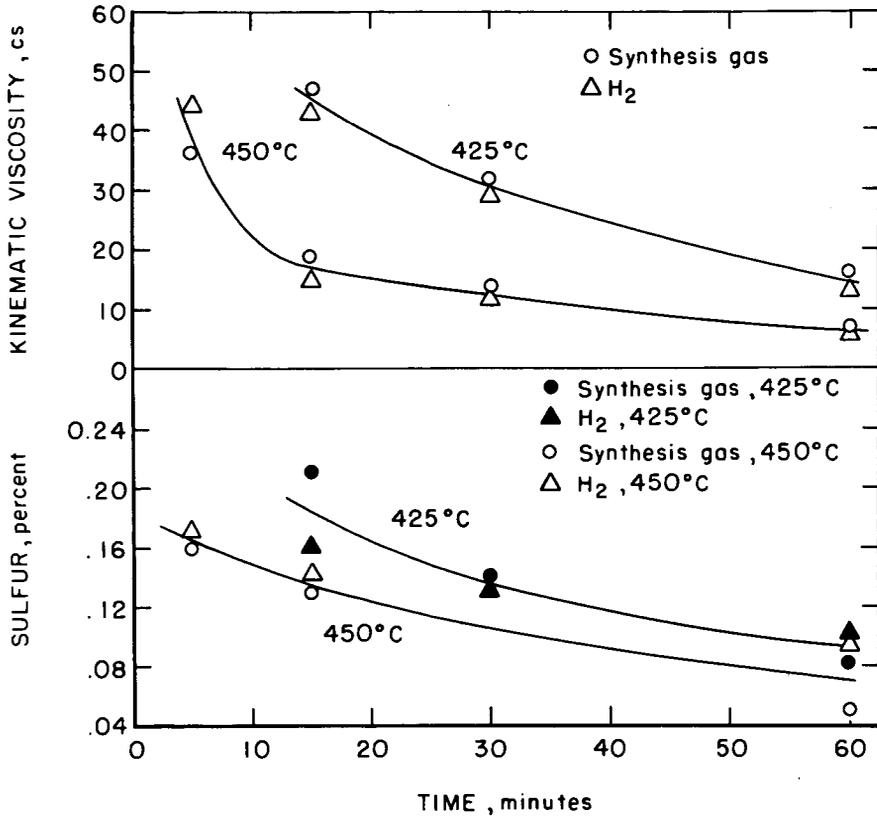


Figure 2 - Kinematic viscosity and sulfur content vs reaction time.

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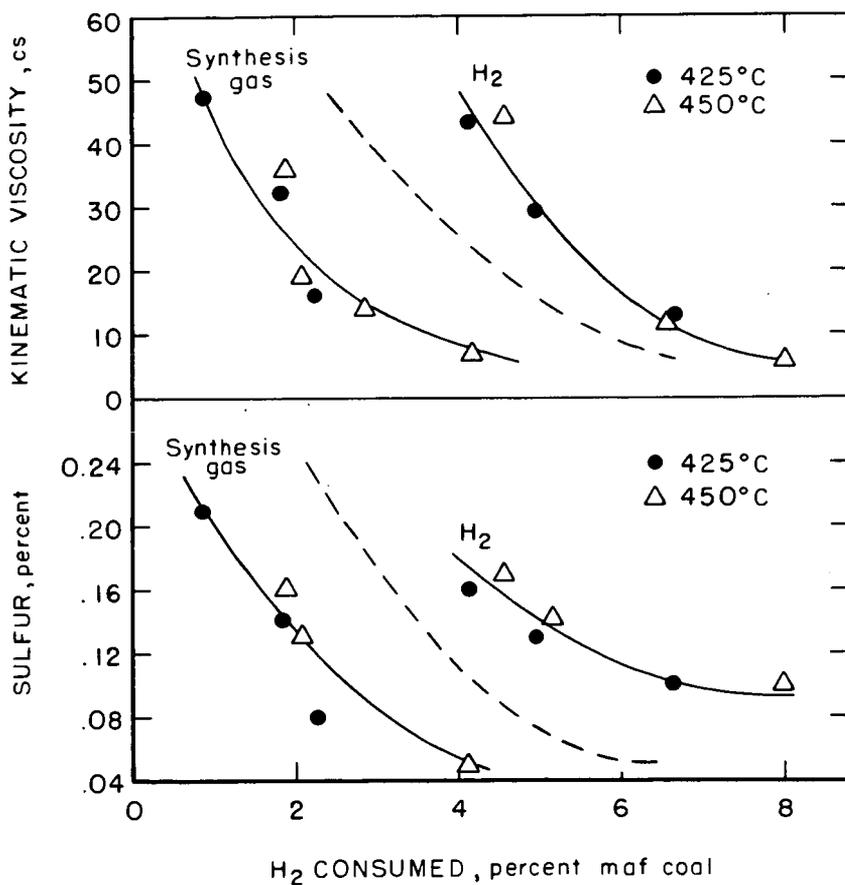


Figure 3- Change of properties with H₂ consumption.

