

EVALUATION OF MORDENITE CATALYSTS FOR PHENANTHRENE HYDROCRACKING

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INTRODUCTION

H-mordenite, in combination with hydrogenation catalysts, has been used in hydrocracking of different types of hydrocarbons. Voorhies and Hatcher¹ and Beecher et al.² used pd-H-mordenite in the study of kinetics of hydrocracking of C₆, C₈ and C₁₀ paraffinic and naphthenic hydrocarbons. The hydrogen mordenite used had a SiO₂/Al₂O₃ of about 10. The reactions were found to be of first order with respect to hydrocarbon concentration and the activation energies of hexane, cyclohexane, n-decane and Decalin were found to be 48, 31, 33 and 25 kcal./mole respectively. Beecher et al.² also used hydrogen mordenite having a SiO₂/Al₂O₃ of greater than 50 in combination with palladium in the hydrocracking of n-decane and Decalin. The aluminum deficient catalyst combination was found to be over 4 times as active as pd-H-mordenite combination. Aluminum deficient H-mordenite (SiO₂/Al₂O₃ = 64) was also found to be more active in cumene cracking by Eberly and Kimberlin³. Qader et al.^{4,5} studied the hydrocracking of naphthalene and anthracene over catalysts containing H-mordenite (SiO₂/Al₂O₃:10) and oxides and sulfides of Co, Mo, Ni and W. The reactions were found to be of first order with respect to hydrocarbon concentration and the activation energies of naphthalene and anthracene hydrocracking were found to be 30.5 and 28.6 kcal./mole respectively. The anthracene hydrocracking data was also found to be compatible with the dualsite mechanism according to the Langmuir-Hinshelwood model. The hydrocracking of phenanthrene over catalyst combinations containing H-mordenites of 10, 50 and 100 silica-alumina ratios is presented in this paper.

EXPERIMENTAL

Phenanthrene of over 99.8 percent purity was hydrocracked in a batch stirred tank reactor of 1-litre capacity, shown in Figure 1. Twenty grams of phenanthrene, 7.5 grams of H-mordenite or silica-(low) alumina and 2.5 grams of WS₂ were used in each experiment. Hydrocracking was carried out in the temperature range 400°-500°C at a constant initial (cold) pressure of 1800 psi. The final (hot) pressures varied between 3000 and 3500 psi. The reactants and catalysts were heated to the experimental temperature in 25-35 minutes and the time when the temperature reached the experimental temperature was taken as zero reaction time as shown in Figure 2. The conversions at zero reaction times were determined by cooling the products immediately after the temperature reached the experimental temperature. It took 1-2 minutes to cool the products to below 300°C in all experiments. It was assumed that no reaction took place during the cooling cycle. Zero reaction time hydrocracking conversions varied between 1 and 5 weight percent of phenanthrene under the experimental conditions employed. Experiments were conducted at reaction times of zero time (as defined above), zero time + 20, zero time + 30 and zero time + 60 minutes. The conversions obtained in between zero reaction time and zero time + 60 minutes were used for evaluation of mechanisms and kinetics. The volume of initial hydrogen used in the reaction and the product gases were measured by a wet gas meter. The liquid product and the spent catalyst were recovered by washing all the reactor parts with acetone.

In experiments designed for calculating weight balances, a weighed quantity of Tetralin was used for recovering the liquid product and catalyst. Catalyst was then separated from the liquid by filtration, washed with acetone and dried at 110°C. The weight of the liquid product was then obtained by difference.

$$\text{Weight of liquid product} = (\text{weight of Tetralin} + \text{Liquid Product} + \text{Catalyst as recovered from the reactor}) - (\text{Weight of initial Tetralin used for washing} + \text{weight of dried spent catalyst}).$$

The weight of C₁-C₄ gases formed was obtained from total volume of gaseous product and gas composition. The difference between initial hydrogen used in the reaction and hydrogen present in product gas was taken as hydrogen consumed in the reaction. The analyses of liquid and gaseous products were done by gas chromatographic techniques. Since phenanthrene molecule contains 14 carbon atoms, all compounds in the product containing 13 carbon atoms or less were taken as cracked products for calculating hydrocracking conversions. The mole percent hydrocracking conversions were obtained from liquid product analyses.

$$\text{Mole percent hydrocracking conversion} = (\text{Sum of mole percentages of all components of the liquid product which is equal to 100}) - (\text{Sum of mole percentages of all components of the liquid product containing 14 carbon atoms}).$$

This was done on the assumption that there will be no change in the liquid moles during the reaction since each mole of phenanthrene can yield only one mole of each component of the liquid product. The higher compounds reported include liquid product components which come out in the chromatographic analysis after phenanthrene and coke.

COKE DETERMINATION

The fresh and spent catalysts were heated in a muffle furnace at 600°C for 3 hours and the weight losses were determined. The difference between the weight losses of each used catalyst and the fresh catalyst was taken as coke formed during the reaction.

RESULTS AND DISCUSSION

Reaction Mechanism:

Hydrocracking of phenanthrene involves three main reaction steps of hydrogenation, isomerization and cracking as indicated by the product distribution data given in Table I. Phenanthrene first gets hydrogenated to di-, tetra- and octa-hydrophenanthrenes. The hydrophenanthrenes, then get isomerized to C₁₄ isomers. C₁₄-isomers contain the same number of carbon atoms (14) as hydrophenanthrenes and they are formed from tetra- and octahydrophenanthrenes by the skeletal rearrangement of saturated six member rings of the latter to saturated five member rings with methyl groups attached to them. The C₁₄-isomers contain one or two saturated five member rings. This skeletal rearrangement is analogous to the isomerizat-

ion of hydroanthracenes to C₁₄-isomers as reported by Qader et al.⁵. The third reaction step is the hydrocracking of hydrophenanthrenes and C₁₄-isomers to lower molecular weight compounds. The product distribution data given in Table I indicates that the initial products of hydrocracking are C₁₃-isomers and naphthalenes. C₁₃-isomers contain 13 carbon atoms and one five member saturated ring in the molecule and they are formed from C₁₄-isomers by demethylation of the latter. The alkylnaphthalenes and naphthalene are formed by the hydrocracking of hydrophenanthrenes, and C₁₄- and C₁₃-isomers. The formation of naphthalenes and tetralins as the initial products of hydrocracking suggests that cracking is taking place in one of the side benzene rings of the hydrophenanthrenes, and C₁₄- and C₁₃-isomers. As cracking proceeds further, indans and alkylbenzenes are formed in the product. This suggests that indans and alkyl benzenes are formed from naphthalenes and tetralins by the occurrence of hydrogenation, isomerization and cracking reactions as reported earlier by Qader et al.⁴. The product distribution data obtained in this work suggest that phenanthrene hydrocracking takes place through the occurrence of a multistep mechanism of hydrogenation, isomerization and cracking as shown in Figure 3. The reaction is a very complex one and the mechanism presented in Figure 2 represents only the gross hydrocracking pattern. Somewhat similar mechanisms were earlier reported by Sullivan et al.⁶ and Rumohr and Kölling⁷. Sullivan et al.⁶ hydrocracked phenanthrene over a nickel sulphide on silica-alumina catalyst and found that the reaction took place partly by a similar mechanism as shown in Figure 3 and partly by two other mechanisms. Rumohr and Kölling hydrocracked phenanthrene over a nickel on alumina catalyst and reported that the reaction took place by a mechanism somewhat similar to the one shown in Figure 3.

KINETICS OF HYDROCRACKING

During hydrocracking, phenanthrene gets hydrogenated to hydrophenanthrenes which subsequently get isomerized to C₁₄-isomers. The hydrophenanthrenes and C₁₄-isomers will then crack to lower molecular weight compounds. All compounds of the product containing less than 14 carbon atoms are taken as cracked products in the calculation of hydrocracking conversions. The conversion data were evaluated by a simple first order rate equation (1) where "x" is mole fraction conversion of phenanthrene

$$\ln (1-x) = -KT + Q \quad (1)$$

(mixture of phenanthrene, hydrophenanthrenes and C₁₄-isomers) and Q is a constant. The plots of equation (1) shown in Figures 4 and 5 indicate that the order of hydrocracking reaction is one with respect to phenanthrene concentration at constant hydrogen pressure. The first order rate constants were used in calculating Arrhenius activation energies as shown in Figure 6. Activation energies of 20.8 and 35.3 kcal./mole were obtained in the hydrocracking of phenanthrene over H-mordenite (10) + WS₂ and Silica-(low) alumina + WS₂ catalysts respectively. The activation energies indicate that the hydrocracking reaction is predominantly controlled by chemical processes. The first order rate constants of phenanthrene obtained over Mordenite and Silica-alumina catalyst systems were found to be represented by equations (2) and (3) respectively.

$$K_m = 2.6 \times 10^2 e^{-20,800/RT} \text{ min.}^{-1} \quad (2)$$

$$K_{SA} = 7.3 \times 10^6 e^{-35,300/RT} \text{ min.}^{-1} \quad (3)$$

ACTIVITIES OF CATALYSTS

Activities of catalysts depend upon reaction conditions and nature of reactants. Activities of catalysts can be evaluated and compared by reaction rates calculated from conversion data. The rate of a chemical reaction is very much influenced by the catalyst activity and it is necessary to keep the catalyst activity same throughout the reaction. In hydrocracking coke deposition takes place on the catalyst and reduces the available active sites which in turn reduces the activity. A large excess of catalyst is used in this work to insure availability of sufficient number of active sites during the reaction. Conversion data obtained on four different catalysts are shown in Figure 7 and the first order rate constants are used to represent catalyst activities. The activities of the catalysts varied in the order H-M-50 + WS₂ \approx H-M-100+WS₂ > Silica-(low) alumina + WS₂ > H-M-10 + WS₂ as shown in Table II. The activity of mordenite + WS₂ catalyst system almost doubled when the silica-alumina ratio of mordenite increased from 10 to 50. The activities of mordenites with silica-alumina ratios of 50 and 100 were found to be same. The aluminum deficient mordenites were earlier found to be more active in the hydrocracking of n-decane and Decalin². Though activity increased with silica-alumina ratio, the phenanthrene hydrocracking mechanism remained same as indicated by the product distribution data given in Table III.

COKE FORMATION

Conversion data shown in Figure 2 indicate that most of the coke was formed during initial stages of the reaction. After the deposition of initial coke, the activity of the catalyst probably gets equilibrated. This appears to be happening at the zero reaction time and the increase in coke deposition after the zero time is not very high. The coke data shown in Figure 8 indicate that the mordenite based catalysts produce less coke when compared to silica-alumina based catalyst. The silica-alumina ratio of the mordenite appear to be having some influence on coke yield. Catalysts with silica-alumina ratios of 50 and 100 yielded more coke when compared to catalyst with silica-alumina ratio of 10.

REACTIVITIES OF HYDROCARBONS

The reactivities of different polynuclear aromatic hydrocarbons are compared by their first order rate constants as shown in Figure 9 and Table IV. The data show that phenanthrene is less reactive when compared to naphthalene and anthracene and more reactive than pyrene. The reactivities varied in the order anthracene > naphthalene > phenanthrene > pyrene.

ACKNOWLEDGMENT

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LITERATURE CITED

- Voorhies, Jr., A., Hatcher, Jr., W. J., Ind. Eng. Chem. Prod. Res. Develop., 8, 361 (1969).
- Beecher, R., Voorhies, Jr., A., Eberly, Jr., P., Ind. Eng. Chem. Prod. Res. Develop., 7, 203 (1969).
- Eberly, P. E. and Kimberlin, Jr., C. N., Ind. Eng. Chem. Prod. Res. Develop., 9, 335 (1970).
- Qader, S. A., Sridharan, R., Hill, G. R., Abstracts, The Second North American Meeting of Catalysis Society, Houston, Texas, p. 75 (1971).
- Qader, S. A., Chun Chen, L. and Mcomber, D. B., 165th National Meeting, American Chemical Society, Division of Petroleum Chemistry, preprints, 18, No. 1, 60 (1973).
- Sullivan, R. F., Egan, C. J., Langlois, G. E., J. Catalysis, 3, 183 (1964).
- Rumohr, V. C. and Kölling, G., Erdol und Kohle-Erdgas-Petrochemie Vereinigt mit Brennstoff-Chemie, 25, No. 6, 309 (1972).

TABLE I. HYDROCRACKING PRODUCT DISTRIBUTION OF PHENANTHRENE
PRESSURE: 1800 PSI (COLD)

Catalyst	WS ₂ (2.5 gram)	H-Mordenite (7.5 gram)	WS ₂ (2.5 gm) +H-Mordenite (7.5 gram)	
			400 0+5	450 0+10
Temperature, °C	400	500	400	450
Reaction Time, Mins.	0+5	0+30	0+5	0+10
<u>LIQUID PRODUCT</u>				
<u>COMPOSITION, WT. %</u>				
Phenanthrene	66.89	82.04	40.37	64.00
Hydrophenanthrenes (Di-, Tetra-, and Octa-)	29.17	10.54	51.70	25.64
Hydrophenanthrene isomers (C ₁₄)	2.68	3.01	4.21	5.22
Hydrophenanthrene isomers (C ₁₃)	0.70	0.50	0.41	0.76
Naphthalenes and Tetralins	0.56	3.13	2.99	3.00
Indans	nil	0.78	0.32	0.11
Alkylbenzenes and benzene	nil	nil	nil	1.27

TABLE II. ACTIVITIES OF CATALYSTS
TEMPERATURE = 450°C
PRESSURE = 1800 psi (cold)

<u>Catalyst</u>	<u>First Order Rate Constant, Sec.⁻¹</u>
H-M-10+WS ₂	12.8 x 10 ⁻⁵
H-M-50+WS ₂	21 x 10 ⁻⁵
H-M-100+WS ₂	21 x 10 ⁻⁵
Silica-(low) Alumina + WS ₂	17 x 10 ⁻⁵

TABLE III. HYDROCRACKING PRODUCT DISTRIBUTION OF PHENANTHRENE
PRESSURE = 1800 psi (cold)

Catalyst	H-M-10+WS ₂	H-M-50+WS ₂	H-M-100+WS ₂
Temperature, °C	400	425	400
Reaction Time, Mins.	0+5	0+5	0+5
<u>LIQUID PRODUCT COMPOSITION, WT. %</u>			
Phenanthrene	40.37	81.95	74.90
Hydrophenanthrenes (Di-, Tetra-, and Octa-)	51.70	15.36	20.19
Hydrophenanthrene isomers (C ₁₄)	4.21	1.31	0.97
Hydrophenanthrene isomers (C ₁₃)	0.41	0.11	0.48
Naphthalenes and Tetralins	2.99	1.27	2.74
Indans	0.32	nil	0.72
Alkylbenzenes and Benzene	nil	nil	nil

TABLE IV. REACTIVITIES OF HYDROCARBONS

Hydrocarbon	TEMPERATURE: 450°C	First Order Rate Constant, Sec. ⁻¹
	PRESSURE: 1800 PSI (COLD)	
Anthracene		16.5 x 10 ⁻⁵
Naphthalene		14.3 x 10 ⁻⁵
Phenanthrene		12.8 x 10 ⁻⁵
Pyrene		5 x 10 ⁻⁵

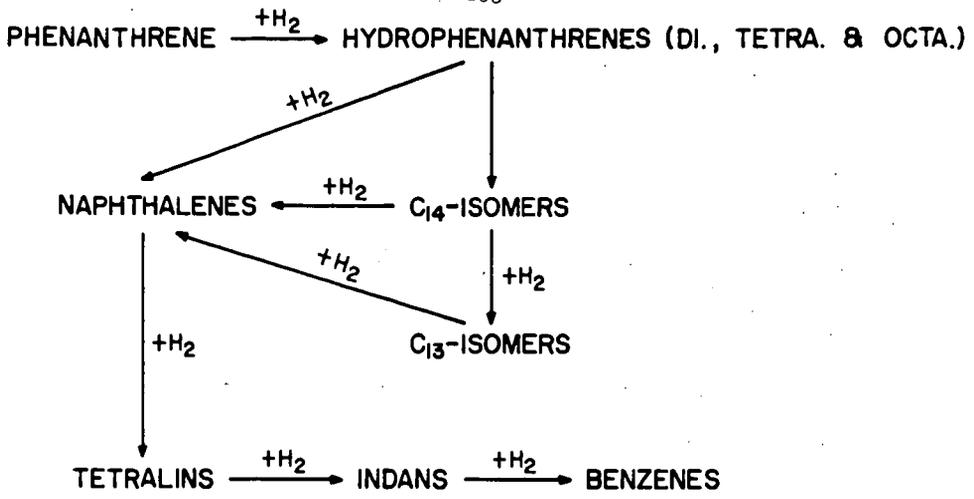
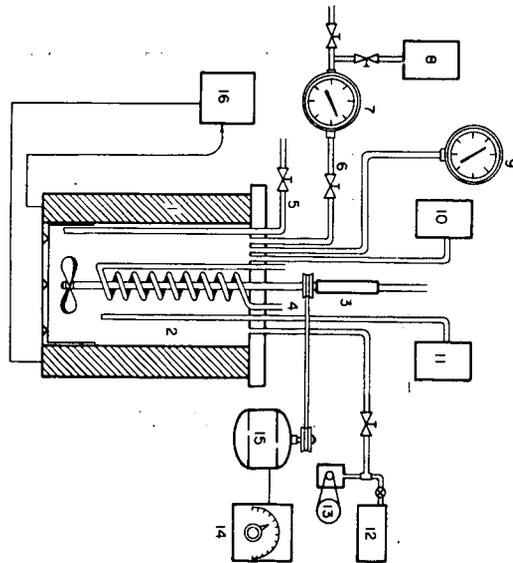


FIGURE 3. HYDROCRACKING MECHANISM OF PHENANTHRENE

FIGURE 1. BATCH STIRRED TANK REACTOR ASSEMBLY.



1. Heating jacket.
2. Thermowell.
3. Magnetic drive assembly.
4. Cooling coil.
5. Liquid sampling line.
6. Gas sampling line.
7. Flow meter.
8. Gas chromatograph.
9. Pressure gage.
10. Pressure recorder.
11. Temperature recorder.
12. Hydrogen tank.
13. Vacuum pump.
14. Stirrer controller.
15. Motor.
16. Temperature controller.

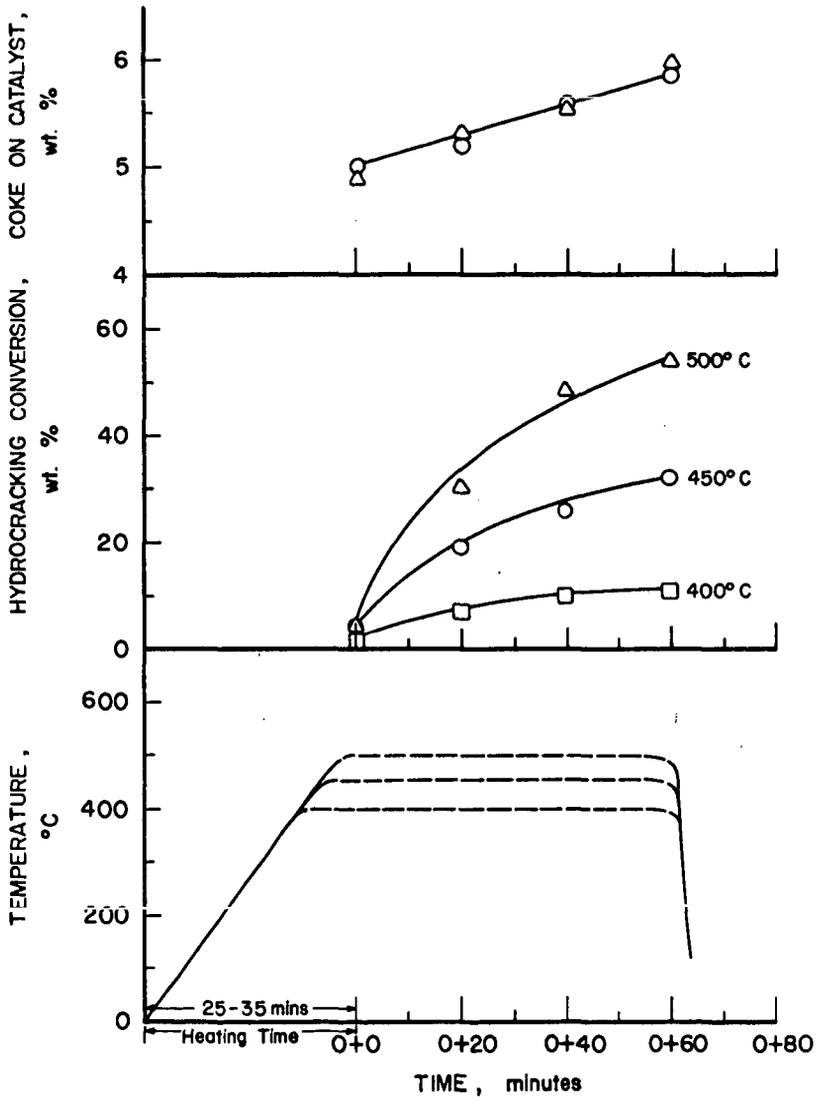


FIGURE 2. HEATING TIME - REACTION TIME - CONVERSION - COKE DEPOSITION

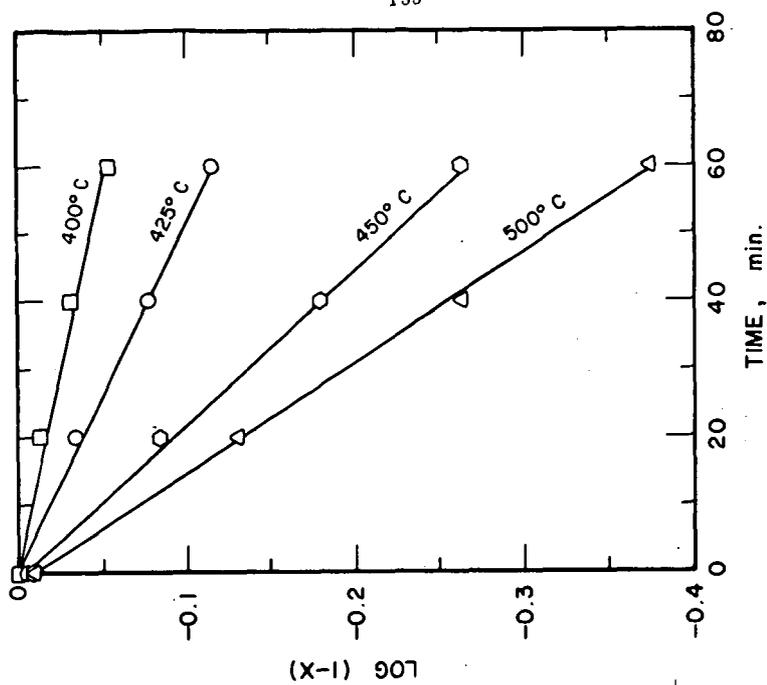


FIGURE 5. FIRST ORDER PLOTS-SILICA-(LOW) ALUMINA + WS_2

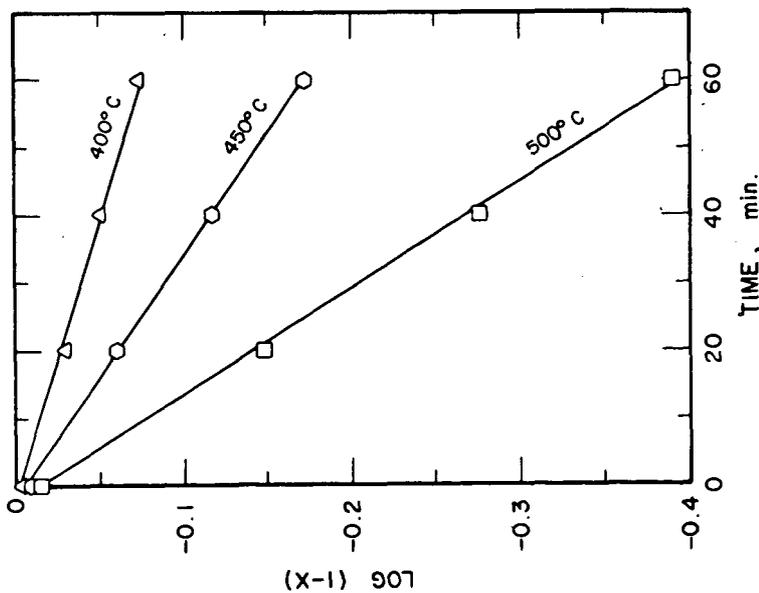


FIGURE 4. FIRST ORDER PLOTS-H-M-10+ WS_2

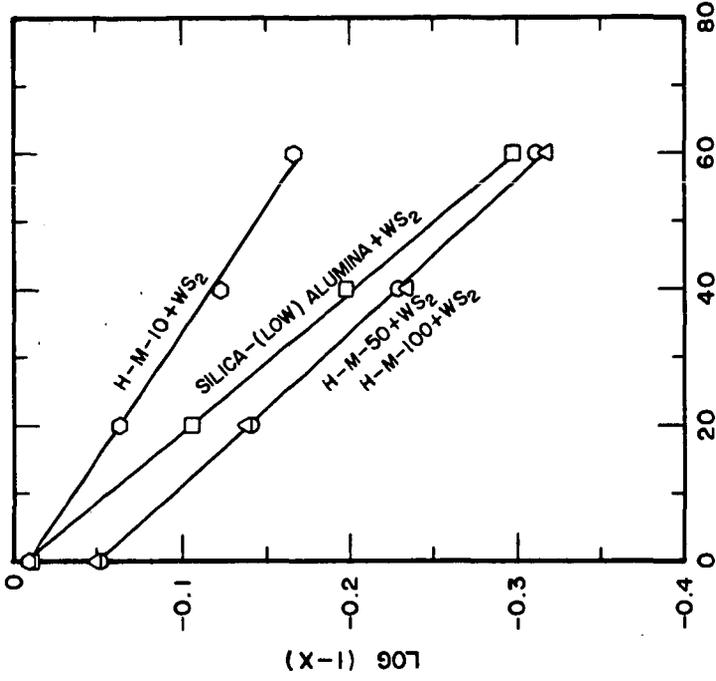


FIGURE 7. ACTIVITIES OF CATALYSTS
TEMPERATURE: 450°C
PRESSURE: 1800 PSI (COLD)

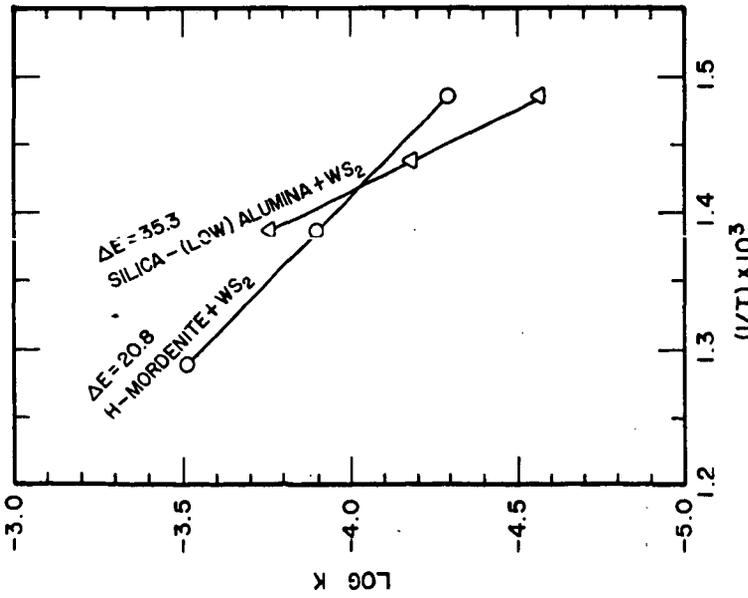


FIGURE 6. ARRHENIUS PLOT

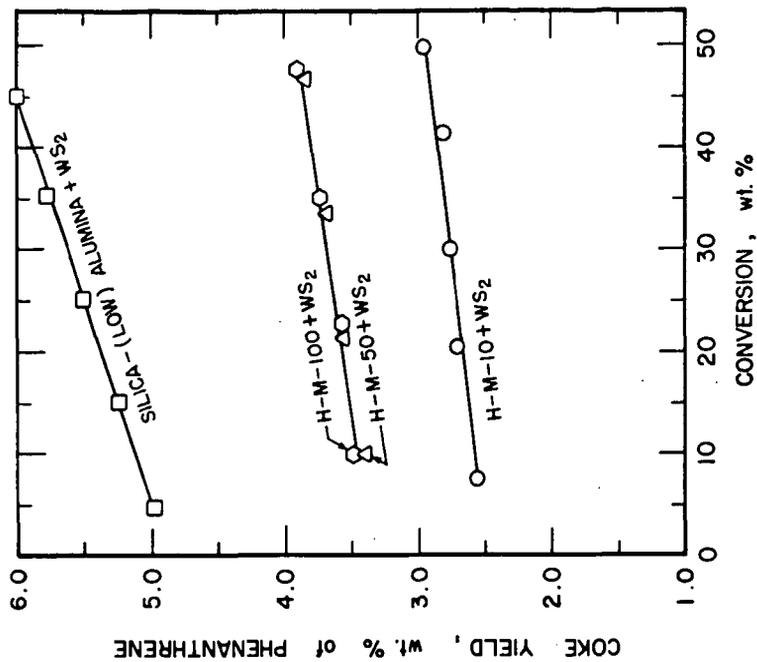


FIGURE 8. COKE YIELD DATA
TEMPERATURE: 450°C
PRESSURE: 1800 PSI (COLD)

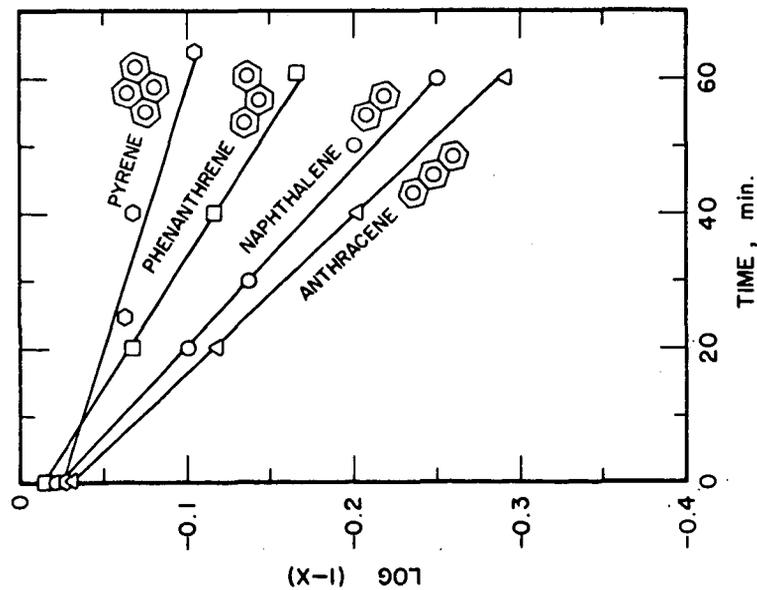


FIGURE 9. REACTIVITIES OF HYDROCARBONS
TEMPERATURE: 450°C
PRESSURE: 1800 PSI (COLD)

COAL TAR AND PETROLEUM PITCHES AS BINDERS
FOR PREBAKED ELECTRODES

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INTRODUCTION

It has been shown that improved binders for Soderberg electrodes can be made by incorporating a rubber reinforcing grade of carbon black in low grade coal tar pitch or a residue from catalytic cracking of petroleum. At the concentration used (1-1.5% of the paste) carbon blacks cannot function merely as a partial replacement for coke fines. The high surface area, small particle size reinforcing blacks improve the homogeneity and mechanical stability of the binder-coke mixture by preventing the separation of oily components at high temperatures and apparently have a catalytic effect on polymerization and condensation reactions associated with coking of the binder.

A cracked petroleum pitch containing carbon black has also been compared to coal tar pitch in a prebaked electrode formulation. In the manufacture of prebaked electrodes, sized calcined coke and/or anthracite aggregate is mixed with 20 to 25% of coal tar pitch at 100-150°C using a hydraulic ram press. A small amount of paraffinic mineral oil is added to the mix to act as a lubricant during extrusion. Extruded electrodes are cooled in a water bath, then packed in sand and baked in a gas-fired pit furnace. The temperature in the furnace is increased gradually over a period of about 30 days to a maximum of 950-1000°C. After baking, the electrodes are cooled, repacked in calcined coke, and graphitized by heating to 1500-3000°C.

The coking characteristics needed in a binder for prebaked electrodes are generally similar to those for Soderberg paste, though lower paste fluidity is adequate for prebaked electrodes: while the paste must be fluid enough to permit forming by extrusion, it is not necessary or desirable that it flow under its own weight.

EXPERIMENTAL

The properties of a coal tar pitch (K) suitable for the manufacture of prebaked electrodes are given in Table 1 along with those of three petroleum binders. Binder H was prepared by dispersing 2.5% of fluffy (unpelletized) ISAF black in the pitch by mechanical stirring. Pitches G and J were made via a colloidal dispersion of commercial pelletized SRF carbon black in an aromatic oil, followed by distillation in vacuo, as previously described.

Thermogravimetric Analyses

Many electrode manufacturers use thermogravimetric analysis (TGA) of the binder to establish the temperature cycle for baking electrodes so that the rate of evolution of hydrocarbon vapours can be controlled. Too rapid emission of gases may cause electrodes to crack during the baking operation. Since the vapours are burned in the furnace

pit and contribute heat to the baking process, a moderate rate of volatilization is required to provide good temperature control. According to a common laboratory procedure, a weighed sample of pitch is placed on a balance pan enclosed in a furnace, the temperature of which is increased to 650°C over a period of 10 hours under nitrogen, and the loss in weight is determined at several temperatures.

The results of coking tests carried out by this procedure (TGA No. 1) on coal tar pitch K and petroleum binder H are shown in Figure 1. Although the initial temperature for evolution of volatiles was about 100°C higher for H than for K, the maximum rate of volatilization (slope of the linear part of the thermogram) of H was greater, and above 600°C it lost weight at a faster rate than K. Rapid loss in weight and a low carbon residue by TGA are generally considered to indicate a tendency to form a porous electrode. However, some doubt remained about the validity of this accelerated TGA test; as noted above, when electrodes are baked commercially, the temperature is raised much more slowly.

A TGA test (No. 2) was carried out at a much lower heating rate. Samples of binder in crucibles were heated for 22 hours in a nitrogen atmosphere at each of seven temperatures from 250 to 800°C, total heating time: 154 hours. After each period, the crucibles were removed from the furnace, cooled in a desiccator, and weighed. The results (Figure 2) differed markedly from those obtained by rapid heating. The coal tar pitch still began to vaporize at a lower temperature than the petroleum pitches G and H, but the maximum rate of volatilization was about the same for all. The different shape of the initial part of the curve for pitch K was shown previously by vacuum distillation analysis to be due to its higher content of non-coke forming light ends as compared to cracked petroleum pitch binders⁽¹⁾.

After slow heating to 800°C, the weight of residue was virtually the same for all pitches. The amount of coke was 69-72% of the binder, as compared to 52-60% by the conventional isothermal coking value test (2.5 hours at 550°C) and the rapid heating TGA method. This is in agreement with Charette and Girolami⁽²⁾ and Martin and Nelson⁽³⁾, who observed that the amount of coke from some coal tar pitches varied inversely as the rate of heating, since slow heating favours condensation and polymerization over cracking and volatilization. Heating rate has a greater effect on cracked petroleum pitch containing carbon black than on coal tar pitch: the difference in the amount of coke from slow and fast heating TGA tests was larger for H (72 vs 52%) than for K (69 vs 60%). This can undoubtedly be explained by the higher proportion of distillable coke forming components in a cracked petroleum residuum as determined by vacuum distillation and analysis of narrow cuts⁽¹⁾.

A third series of TGA tests were carried out to determine the effect of the presence of petroleum coke aggregate. Girolami⁽⁴⁾ reported that coal tar pitch has a higher apparent coking value when heated in the presence of calcined coke particles than when heated alone. In our test, (TGA No. 3) mixtures containing 23% binder and 77% calcined coke flour* were heated for 22 hours at each of six temperatures

* Coke I, Figure 4

between 300 and 800°C. As indicated in the next section, the proportions of binder and coke used were about optimum for prebaked electrodes made from this aggregate.

The results of the tests, shown in Figure 3, were quite different from those observed for the binders alone at the same heating rate. The initial evolution of volatiles from all of the mixtures occurred at the same temperature (300°C) but at about double the rate observed for the pure binders at 300-450°C, indicating interaction between the pitch and coke. At the same final temperature (800°C) the weight loss was higher than when the binders were heated alone, a result in disagreement with the observations of Girolami, and of Martin and Nelson above. The cracked pitch H containing only 2.5% carbon black had an extremely low effective coking value (29), whereas the one with 5% carbon black and the coal tar pitch both had about 50. Conclusions are that the additional 2.5% carbon black in G is of benefit during the baking procedure and this is borne out by the electrode test data presented in the following section.

Evaluation of Test Electrodes

The three petroleum binders and coal tar pitch, inspections of which are given in Table 1, were compared in several prebaked electrode formulations containing 21 to 27% binder. Two calcined coke aggregates were used, with particle size distributions as shown in Figure 4. About 2% extrusion oil based on the coke was added to the mixture. The coke and binder were stirred in a sigma bladed mixer at about 160°C and molded at 130°C under a pressure of 5,000 psig. After cooling to 95°C, the samples were removed from the molds, measured and weighed. The binders all gave similar molded green mix densities. The green electrodes were packed in calcined coke in stainless steel molds for baking, which was carried out in a 48 hour controlled temperature cycle. The electrodes were held at the maximum temperature of 1000°C for 2 hours. After cooling in the furnace, they were removed from the molds, brushed free of coke scale, measured and weighed, then machined to obtain specimens 2.5 inches in diameter and 3 inches long which were evaluated for density, electrical resistivity, and compressive strength. Experimental data for the mixes containing the optimum amount of binder (22-23 wt %) are summarized in Tables 2 and 3. The average loss of volatiles from cracked pitch (5.0% SRF black) using the two coke aggregates was the same as for the coal tar pitch (33-34%), but the others containing only 2.5% black lost 37 and 40% in weight respectively.

Table 4 gives a comparison of effective coking values obtained by five procedures: the isothermal coking test, three laboratory TGA tests and during baking of electrodes. The isothermal test, which agrees with the Norske method⁽²⁾, and the rapid heating TGA procedure (No. 1) both gave less coke than when electrodes were baked. This result confirms results reported by Martin and Nelson⁽³⁾. The slow heating TGA procedure (No. 2) on the binders alone gave a coke yield somewhat higher than that found in the baking tests. However, TGA test No. 3 on the binder/coke mixture produced substantially less coke than by electrode baking, a result that is not susceptible to a plausible explanation.

It appears that thermogravimetric analysis of the binder alone at a very slow heating rate can be used to predict the approximate yield of coke from coal tar pitch binders and possibly from cracked petroleum binders containing the optimum amount (about 5%) of carbon black. However, it must be concluded that in other cases a reliable indication of performance is obtainable only by preparing and baking test electrodes.

Figure 5 shows the density of baked test electrodes as a function of the amount of coked binder (coke residue, wt %, x binder content). Each curve has a maximum corresponding to the optimum amount of coked binder. An electrode made using pitch G with the optimum carbon black content had a maximum baked electrode density at least as high as coal tar pitch binder.

As expected, the compressive strength of baked test electrodes varied directly with electrode density, and for the same coke aggregate the relationship is independent of the origin of composition of the binder (Figure 6). The indicated higher average strength of electrodes made from coke I may be due to the denser grading of this aggregate in the coarse fractions.

The electrical resistivity of baked electrodes decreased with increasing electrode density as shown in Figure 7. Because coke II is more densely graded in the fine fractions, electrodes made from this aggregate had lower electrical resistivity than those made from coke I, especially at low electrode densities.

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LITERATURE CITED

- (1) King, L. F. and Robertson, W. D., Fuel, Lond. 1968 47, 197
- (2) Charette, L. P. and Girolami, L., Fuel, Lond. 1958 37, 382
- (3) Martin, S. W. and Nelson, H. W., Ind. Eng. Chem. 1958 50, 33
- (4) Girolami, L., "Effect of Aggregate on the Coking of Binder in Petroleum Coke-Pitch Mixtures;" paper presented at symposium on Non-Fuel Uses of Coal, American Chemical Society, Cincinnati, Ohio, meeting, January 13-18, 1963.

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR PREBAKED ELECTRODES

PROPERTIES OF BINDERS FOR PREBAKED ELECTRODES

COMPOSITION WT %	Coal Tar		Cracked Petroleum Pitch	
	Pitch K	G	H	J
VACUUM REDUCED				
CAT CRACKING RESIDUE	85	97.5	97.5	
SRF CARBON BLACK	5		2.5	
ISAF CARBON BLACK				2.5
PROPERTIES				
SOFTENING POINT (C/A) °C	100	97	102	100
DENSITY AT 15°C g/cm ³	1.31	1.23	1.22	1.22
CONING VALUE, WT %	58	52	54	53
BENZENE INSOLUBLE, WT %	31	8	3.5	3.5
DINDLINE INSOLUBLE, WT %	8	5	2.5	2.5
C/H (ATOMIC) RATIO	1.7	1.3	1.3	1.3

Table 1

THERMOGRAVIMETRIC ANALYSES OF BINDERS FOR PREBAKED ELECTRODES BY TGA PROCEDURE NO.1

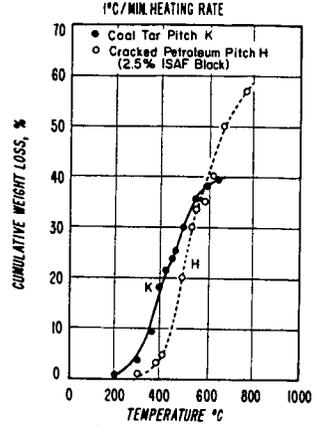


Figure 1

THERMOGRAVIMETRIC ANALYSES OF BINDERS FOR PREBAKED ELECTRODES BY TGA PROCEDURE NO.2

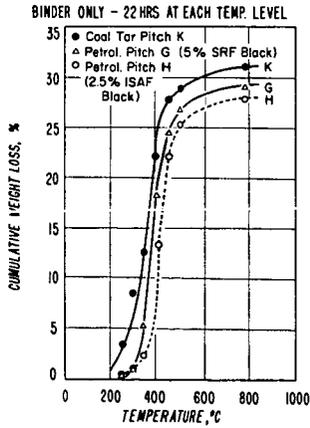


Figure 2

THERMOGRAVIMETRIC ANALYSES OF BINDERS FOR PREBAKED ELECTRODES BY TGA PROCEDURE NO.3

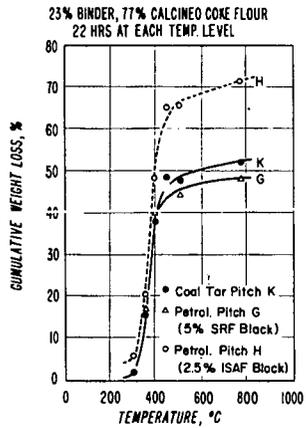


Figure 3

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR PREBAKED ELECTRODES

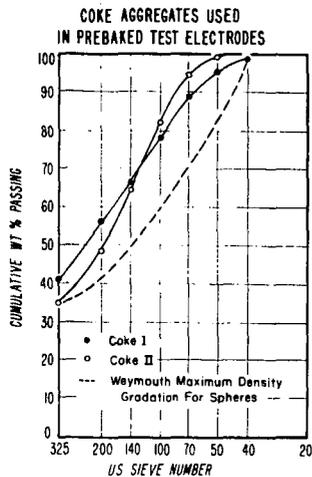


Figure 4

PERFORMANCE OF BINDERS IN PREBAKED ELECTRODES

BINDER	Coal Tar Pitch	Cracked Petroleum Pitch		
		K	H	J
CARBON BLACK IN BINDER	-	5%SRF	25%ISAF	25%SRF
BINDER CONTENT, WT %	23.0	23.0	23.0	23.0
<u>BAKED ELECTRODES</u>				
DENSITY, g/cm ³	1.49	1.50	1.45	1.43
ELECTRICAL RESISTIVITY, 10 ³ ohm cm	1.09	1.08	1.13	1.16
COMPRESSIVE STRENGTH, kg/cm ²	508	543	329	326

*OPTIMUM 2, PARAFFINIC EXTRUSION OIL ADDED IN ADDITION TO BINDER

Table 2

PERFORMANCE OF BINDERS IN PREBAKED ELECTRODES

BINDER	Coal Tar Pitch	Cracked Petroleum Pitch		
		K	H	J
CARBON BLACK IN BINDER	-	5%SRF	25%ISAF	25%SRF
BINDER CONTENT, WT %	23.0	23.0	22.0	22.0
<u>BAKED ELECTRODES</u>				
DENSITY, g/cm ³	1.50	1.46	1.46	1.45
ELECTRICAL RESISTIVITY 10 ³ ohm cm	1.06	1.08	1.08	1.15
COMPRESSIVE STRENGTH, kg/cm ²	467	357	378	221

*OPTIMUM 2, PARAFFINIC EXTRUSION OIL ADDED IN ADDITION TO BINDER

Table 3

EFFECTIVE COKING VALUE OF BINDER PITCHES

BINDER	Coal Tar Pitch	Cracked Petroleum Pitch		
		K	H	J
CARBON BLACK IN BINDER	-	5%SRF	25%ISAF	25%SRF
<u>COKING PROCEDURE</u>				
ISOTHERMAL, 25HR AT 550°C	-	58	52	54
TGA 1 - 10 HR TO 850°C (binder only)	-	60	-	52
TGA 2 - 154HR TO 800°C (binder only)	-	69	71	71
TGA 3 - 132HR TO 800°C (23 binder, 77% coke)	-	48	51	129
ELECTRODE BAKING 48HR TO 1000°C (23 binder, 77% coke)	-	67	66	63

Table 4

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR PREBAKED ELECTRODES

RELATIONSHIP BETWEEN BAKED ELECTRODE DENSITY & COKED BINDER CONTENT

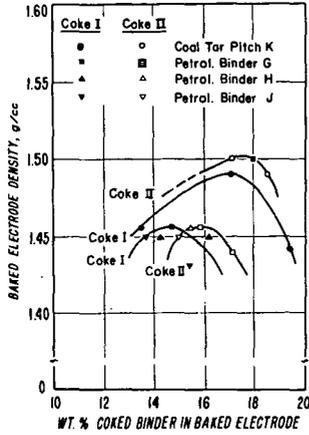


Figure 5

RELATIONSHIP BETWEEN COMPRESSIVE STRENGTH & DENSITY OF BAKED TEST ELECTRODES

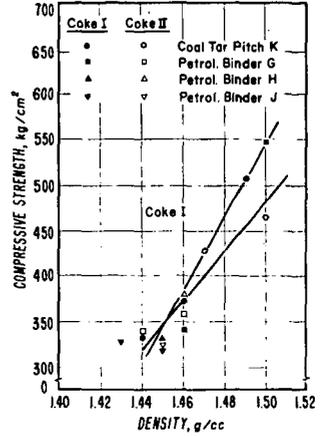


Figure 6

RELATIONSHIP BETWEEN ELECTRICAL RESISTIVITY & DENSITY OF BAKED TEST ELECTRODES

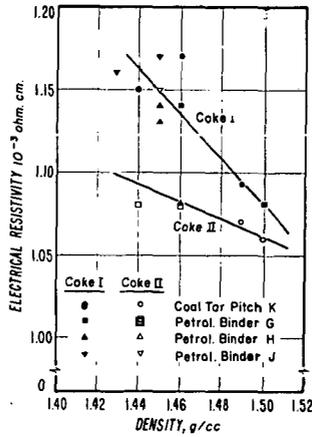


Figure 7

COAL TAR AND PETROLEUM PITCHES AS
BINDERS FOR SODERBERG ELECTRODES

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INTRODUCTION

It was concluded from a previous study⁽¹⁾ that the efficacy of coal tar and petroleum pitches as binders for coke in carbon electrodes is governed mainly by their aromaticity and content of distillable coke precursors. A thermal petroleum pitch containing about the same amount of resins insoluble in quinoline and benzene as coal tar pitch, but no volatile coke formers, was unsatisfactory as an electrode binder⁽²⁾. On the other hand, a vacuum reduced residue from a petroleum catalytic cracking process, though having no C₁ (quinoline insoluble) or C₂ (quinoline soluble, benzene insoluble) resins and few of the other characteristics of coal tar pitch, generally gave laboratory test electrodes having high density and compressive strength.

Parameters affecting the yield of binder pitch from the petroleum catalytic cracking process have been identified. Data obtained by vacuum reduction of catalytically cracked residues are shown in Figure 1. The yield of pitch having a softening point of 95°C is a function of aromaticity, as indicated by the U.S. Bureau of Mines Correlation Index (BMCI), the yield increasing from 6% of an 80 BMCI residue to 30% of a 120 BMCI residue. Figure 2 shows the relationship between aromaticity of the material boiling above 370°C and cracking severity as indicated by feed conversion to gas and naphtha boiling below 221°C.

In aluminum manufacture, inorganic contaminants in either the binder or coke aggregate components of the electrodes in the reduction furnace may show up as impurities in the product, or may accumulate in the molten electrolyte and reduce the current efficiency of the cell. Typical specifications for electrode binder pitches allow a maximum of 0.3% ash. To meet this requirement, it is necessary to remove at least 95% of the catalyst fines (corresponding to all particles larger than about 10 microns) from catalytically cracked residue. Semi-commercial studies showed that this can be accomplished by allowing the solids to settle in tankage at 65°-110°C for 5-10 days per foot of liquid depth.

EXPERIMENTAL

Some Soderberg pastes made with cracked petroleum pitch are mechanically unstable at high temperatures: at 255°C oil components are exuded from the green mix of pitch and petroleum coke aggregate. This was found to be a function of binder content, separation of oil being observed only at the pitch level required to impart adequate flow properties to the paste. Oil bleeding is an undesirable property because of the possibility of leakage from the anode casing in commercial operation. A related phenomenon is a tendency for the green mix to decrease in consistency soon after preparation. Mechanical instability is not normally observed when paste is prepared with coal tar pitch as binder.

Earlier work had indicated that a pitch suitable as an electrode binder could be made by heat soaking a catalytically cracked petroleum residue at about 375°C in the presence of an active carbon catalyst (type CAL, 12-40 mesh, Pittsburgh Coal and Chemical Co. Inc.)⁽³⁾ and the yield also was increased from 25% to 42%. Though it was well known that coarse (thermal) carbon blacks, when added in large quantities to Soderberg paste, may act as a replacement for some of the coke fines⁽⁴⁾, the use of catalytic amounts of high surface area, non-pelletized blacks pre-dispersed in the pitch had not been reported.

The type of carbon black is critical⁽⁵⁾. The most suitable ones are the super abrasion (SAF) furnace blacks, intermediate super abrasion (ISAF), semi-reinforcing (SRF) furnace blacks made by G. L. Cabot Inc. and fast extruding furnace black (FEF) of Columbian Carbon Co. Because of their high surface area, structural characteristics and surface adsorption properties, these rubber reinforcing grade blacks are also effective as stabilizers for Soderberg paste (Table 1). At a concentration of 5% in catalytically cracked petroleum binder (1.5% of the paste) the furnace blacks prevented bleeding of oil and change in consistency of the green mix, whereas the large particle size MT (thermal) black provided no significant improvement in these properties. It is probable that there is also a catalytic effect involving the formation of C₁ and C₂ resins in situ during the carbonization (baking) process. It is important to note that, to be effective, aggregates in commercial pelletized carbon blacks must be broken down into discrete particles. A concentrated suspension of the black in an aromatic distillate (from thermal cracking of gas oil), prepared by mixing in a tank, was passed through a colloid mill, and a quantity sufficient to give the desired carbon black content in the finished binder was blended with the vacuum reduced pitch or with the feedstock to distillation. The blending oil was removed later in vacuo.

When proper dispersion is attained, there is little or no tendency for solids to settle out of pitches containing furnace blacks during hot storage. Frequent circulation of coal tar electrode binder pitch is commonly practiced in the industry to minimize the deposition of benzene and quinoline insoluble components in storage tanks. One micron is reported as the average diameter of quinoline insolubles⁽⁶⁾. Our laboratory data showed that two representative coal tar pitches deposited about half of their C₁ and C₂ resins in 5 to 20 days at 205°C. A cracked petroleum pitch, in which 5% of pelletized SRF black (80 µ particle diameter) had been dispersed by colloid milling, required 330 days at 225°C for settling of 25% of the black.

Flow Properties of Soderberg Pastes

In addition to its other functions, the binder in Soderberg paste must impart the fluidity necessary for flow to all parts of the anode casing. This depends on the gradation of the coke aggregate (which in practice is fixed), the amount of binder and its viscosity.

The flow properties of Soderberg paste are commonly evaluated by an empirical "elongation" test^(3,5). Four samples of paste, pressed into a cylindrical mold and cooled rapidly, are placed on an aluminum test plate - made so that the surface is sloped at an angle of 10° to

the horizontal - and heated in an oven at 255°C for 15 minutes. The plate is then removed from the oven, shock chilled, and the elongation of the samples as a percentage of the original length is calculated. For commercial electrodes, the value desired is approximately 100%, and it varies more or less logarithmically with the binder content. With coal tar pitches, 30 to 35% binder is needed⁽⁷⁾.

Although the addition of a small amount of furnace black to a binder substantially improves the stability of Soderberg paste, it also reduces fluidity. Typical results for two such carbon blacks in catalytically cracked petroleum pitch are shown in Figure 3. Elongation also depends on the particle size of the black (Figure 4). Thermal blacks have a negligible effect on paste fluidity at low concentrations; this is undoubtedly related to their inability to modify the oil bleeding and aging characteristics of the paste.

A study was made of the flow properties of catalytically cracked petroleum pitches containing SRF carbon black and of Soderberg paste made with them. An experimental sample, designated as "Cracked Pitch D" was prepared on a small commercial scale as described above. Another pitch (Blended Pitch E) was prepared in the laboratory. Vacuum reduced (480°C+) bottoms from catalytic cracking, blended with 5 wt % of a 150°C softening point vacuum reduced tar from thermal cracking of gas oil, and a dispersion of SRF carbon black in oil were redistilled in vacuo to remove the oil. These two petroleum pitches are compared in Table 2 with a coal tar pitch binder (F) typical of that used at about 30% concentration in Soderberg paste.

The viscosity of electrode binder pitch is normally measured with a Brookfield viscosimeter at various temperatures and spindle rotation speeds. The rate of shear is high, but not precisely known. This is not important in the case of coal tar pitches which are reported to be Newtonian⁽⁸⁾. Since cracked petroleum pitches were suspected of being pseudoplastic, it was decided to determine viscosity at known shear rates.

Flow properties of binders D, E and F were evaluated in Koppers vacuum capillary viscometers at three temperatures: 107, 135 and 163°C. Data obtained at various shear rates are shown in Figures 5, 6 and 7. While coal tar pitch F was confirmed as being Newtonian throughout, the petroleum pitches were shear sensitive. At the lowest temperature and shear rate D had the lowest viscosity, at 135°C it was intermediate and at 163°C and high shear rate it had the lowest viscosity. Flow indices calculated for D and E were 0.7 and 0.9 (1.0 for F).

In commercial practice, Soderberg paste is cast into blocks about 3.5 x 13 x 1 ft in size and weighing over 5000 lb. The anodes are replenished by placing a block of solidified paste on top, where the temperature is 100-150°C. The paste should flow to all corners of the anode casing under these conditions. The pressure at the bottom of a block of paste due to its own weight is approximately 10^4 dynes/cm². The laboratory elongation test previously described was developed to control the fluidity of Soderberg pastes made with coal tar pitch under average commercial operating conditions. In the laboratory test, the stress causing the paste to flow is about 10^3 dynes/cm² but the

temperature (225°C) seemed much too high. Additional elongation tests done at 205° and 150°C gave the results shown in Figure 8. The binder requirements of the three pitches were as indicated, being based on 80-100% elongation at 255°C. The effect of too little binder on the elongation of the paste is shown by the lowest curve.

To simulate the very low shear rates of commercial operation, a laboratory spreading test was developed. A block of Soderberg paste, 1.5 x 6 x 0.5 inches in size and loaded with steel weights as required, is placed in a shallow steel container (2.5 x 6 x 0.25 inches) and heated in an oven at 150°C. Since the volume of the container was made equal to the volume of the semi-molten block of paste, spreading of the block is complete when the container is filled. Tests were carried out using pastes containing the "optimum" amount of coal tar pitch F, cracked pitch D, and blended pitch E, for periods of 1, 8 and 16 hours: (a) under a load of 0.5 psi which produces a stress of about 10^4 dynes/cm², and (b) under no applied load. The results are shown in Figure 9.

Correlations between Soderberg paste elongation, spreading tests and the apparent viscosity of the binder under similar conditions of temperature and stress are complex. At 255°C and a shearing stress of 10^3 dynes/cm², the apparent viscosities of all three binders tested are so low (0.01 poise) that the binder viscosity probably has little effect on the flow properties of the paste. Under these conditions, it is the amount of binder that has the greatest effect on the fluidity of the paste by controlling the packing of the coke aggregate particles.

In the elongation test at 150°C, there is some indication that the flow of the paste increases as the apparent viscosity of the binder increases, and the same result was observed in the spreading test at 150°C under a load of 0.5 psi (upper curve, Figure 10). It is possible that in this viscosity range (about 1 to 10 poises) the film of binder on the coke aggregate particles is not of sufficient thickness to lubricate them under a stress of 10^3 to 10^4 dynes/cm²; and as the viscosity of the binder is increased, friction between the particles decreases due to the thicker lubricant film.

In the spreading test at 150°C with no applied load (lower curve, Figure 10) flow varies directly as the apparent viscosity of the binder, indicating that at extremely low stress levels, the viscous resistance of the binder has a significant retarding effect on the flow of the paste.

Electrode Performance

The performance of the binders in laboratory scale baked electrodes is summarized in Table 3. The procedure of Jones et al was used⁽⁹⁾. All test data appear satisfactory. For cracked pitch D, the optimum binder content, the elongation at 225°C immediately after preparation and again after aging the paste for 24 hr at 225°C, and the properties of baked test electrodes made from aged and unaged paste are given.

L. Girolami⁽¹⁰⁾ has reported a "saturation" test which involves heating coal tar Soderberg paste in two stages (at 200°C and at 300°C) prior to laboratory coking at the normal temperature of 550°C. The yield of coke was increased by the preheating steps, depending on the fineness of the coke, the soaking temperature and the binder/aggregate ratio. Girolami ascribed this behaviour to displacement of air or other gases adsorbed on the coke aggregate, thus permitting more intimate contact between binder and coke. Our results appear to confirm this finding: the density and compressive strength of electrodes increased significantly after heat soaking of the paste. This has been observed in our laboratory with many petroleum pitches.

A small scale trial of cracked petroleum pitch D was carried out in a commercial Soderberg anode. In spite of the fact that less than the indicated optimum amount of binder was inadvertently used in the paste (26 vs 31%) the performance was satisfactory, the rate of anode consumption being low. The paste on the top of the cell required manual spreading since it would not spread to fill the casing completely by virtue of its own weight. The petroleum binder exhibited extremely low volatility at the ambient temperature, so the amount of vapour above the cell was almost negligible compared to that evolved by coal tar binders.

Upgrading Coal Tar Pitch

Coal tar pitches from different sources are variable in quality. Low grade binders can be improved for Soderberg electrode use by addition of furnace blacks in much the same way as petroleum residua. The improvement is evidenced by increased density and compressive strength of baked test electrodes. Coal tar pitches which are most readily upgraded are those having a relatively low coking value (about 50%) and a quinoline insolubles content of less than 10%. Literature data⁽⁶⁾ indicate that the best coal tar binders contain 10 to 15 wt % of quinoline insoluble resins.

Laboratory inspections and performance data are summarized in Table 4. Addition of 2.5 wt % of a reinforcing black to poor quality coal tar pitches effected a marked improvement in performance. In one case, (A), the elongation of the paste was below the desired value for Soderberg electrodes, but this could be overcome by increasing slightly the amount of binder used. This is shown in B, where the retarding effect of the carbon black on paste flow was compensated for by increasing the binder content from 30.5 to 32%.

ACKNOWLEDGEMENT

The authors wish to acknowledge the assistance of W. D. Horley who carried out the laboratory evaluations and A. J. Hellwig, who assisted in plant production of samples for commercial trial.

LITERATURE CITED

1. King, L. F. and Robertson, W. D., Fuel, Lond. 1968, 47, 197.
2. King, L. F. and Steele, C. T., U.S. Patent 3,173,851, March 16, 1965.
3. King, L. F., U.S. Patent 3,355,377, November 28, 1967.
4. Swallen, L. C. and Nelson, H. W., U.S. Patent 2,527,595, October 31, 1950.
5. King, L. F., Robertson, W. D. and Steele, C. T., U.S. Patent 3,316,183 April 25, 1967.
6. Charette, L. P. and Girolami, L., Fuel, Lond. 1961, 40, 89.
7. Darney, A. "Pitch Binder for Carbon Electrodes" pp 152-161 in Industrial Carbon and Graphite, Society of Chemical Industry: London, 1958.
8. McNeil, D. and Wood, L. J. "The Use of Coal Tar Pitch as Electrode Binder" *ibid.* pp. 162-172.
9. Jones, H. L., Simon, K. W., Wilt, M. H. "An Improved Evaluation of Electrode Binder Pitches Using the Compressive Strength of Electrodes". Paper presented at the Division of Gas and Fuel Chemistry, American Chemical Society, Boston, Mass. meeting April 5-10, 1959.
10. Girolami, L. "Effect of Aggregate on the Coking of Binder in Petroleum Coke - Pitch Mixtures"; paper presented at symposium on non-fuel uses of coals, American Chemical Society, Cincinnati, Ohio, meeting January 13-18, 1963.

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR SODERBERG ELECTRODES

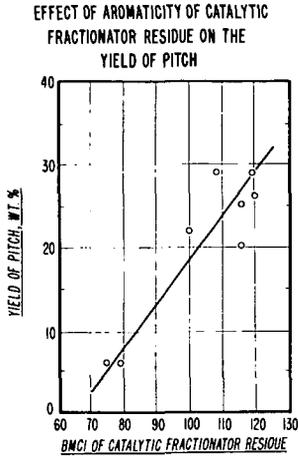


Figure 1

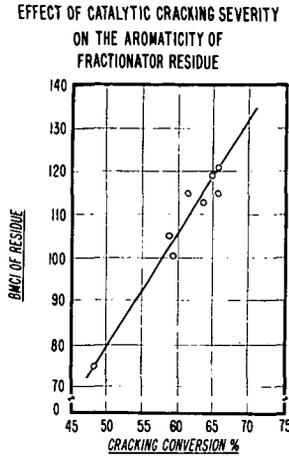


Figure 2

PROPERTIES OF SODERBERG PASTES

BINDER	Coal Tar Pitch (Typical)		Catalytically Cracked Petroleum Pitch			
	None	None	ISAF	SRF	SRF	Thermal
CARBON BLACK IN BINDER						
TYPE			ISAF	SRF	SRF	Thermal
GRADE			23	88	80	470
AVER. PARTICLE SIZE, μ			2.5	5.0	7.5	5.0
WT.						
OPTIMUM BINDER CONTENT, WT. %	28.33	27	31	32	33	30
STABILITY	Good	Poor	Good	Good	Good	Poor
AGEING CHARACTERISTICS	Good	Poor	Poor	Good	Good	Poor
BAKED TEST ELECTRODE COMPRESSIVE STRENGTH, Kg/cm^2	750-450	270-405	400	380	410	370

Table 1

EFFECT OF CARBON BLACK CONCENTRATION IN CRACKED PETROLEUM PITCH ON FLOW PROPERTIES OF SODERBERG PASTE

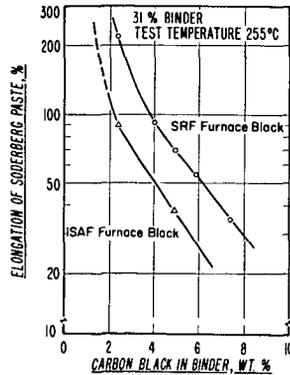


Figure 3

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR SODERBERG ELECTRODES

EFFECT OF PARTICLE SIZE OF CARBON BLACK IN CRACKED PETROLEUM PITCH BINDER ON THE FLOW PROPERTIES OF SODERBERG PASTE

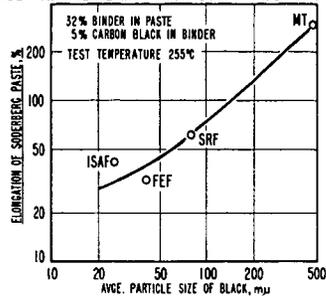


Figure 4

PROPERTIES OF BINDERS FOR SODERBERG ELECTRODES

	Coal Tar Pitch		Petroleum Pitch	
	F	D	E	
COMPOSITION, WT. %				
VACUUM REDUCED				
CAT CRACKING RESIDUE		85	80	
VAC REDUCED THERMAL CRACKING RESIDUE		-	5	
SRF CARBON BLACK		5	5	
PROPERTIES				
SOFTENING POINT (A) °C	82	80	82	
DENSITY AT 15°C, g/cm ³	1.31	1.23	1.24	
COKING VALUE, WT. %	58	54	57	
BENZENE INSOLUBLE, WT. %	22	8	10	
QUINOLINE INSOLUBLE, WT. %	18	6	7	

Table 2

APPARENT VISCOSITY OF ELECTRODE BINDER PITCHES AT 107°C
KOPPERS TYPE VACUUM CAPILLARY VISCOMETER

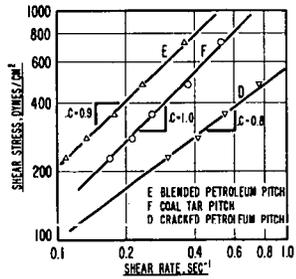


Figure 5

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR SODERBERG ELECTRODES

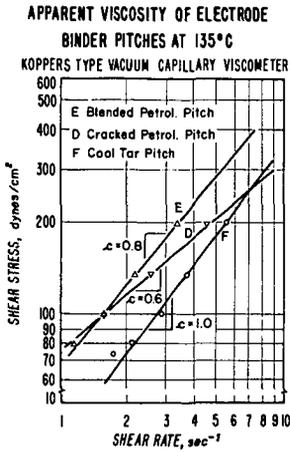


Figure 6

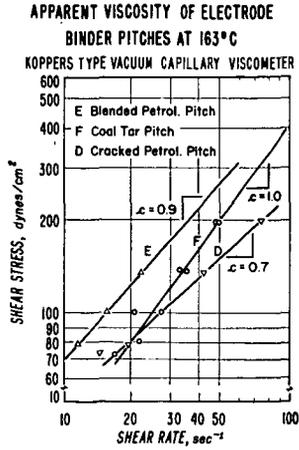


Figure 7

EFFECT OF TEMPERATURE ON THE ELONGATION OF SODERBERG PASTES

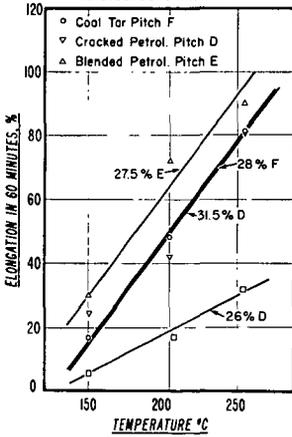


Figure 8

SPREADING OF SODERBERG PASTES AT 150°C

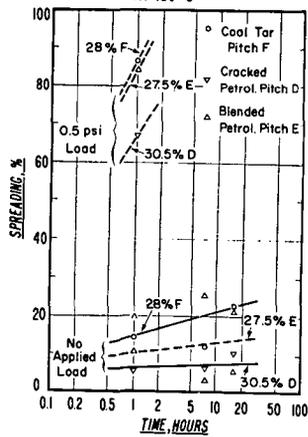


Figure 9

COAL TAR AND PETROLEUM PITCHES AS BINDERS FOR SODERBERG ELECTRODES

RELATIONSHIP BETWEEN SPREADING OF SODERBERG PASTE
& BINDER VISCOSITY

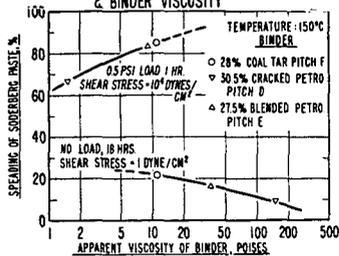


Figure 10

PERFORMANCE OF SODERBERG ELECTRODE BINDERS

Binder	Coal Tar	Petroleum			
	Pitch F	Cracked Pitch D	Blended Pitch E		
SODERBERG PASTE					
BINDER CONTENT, WT. %	28	28	31	33	27.5
ELONGATION AT 255°C, %	82	40	84	181	72
AFTER AGEING	-	52	82	174	-
BAKED ELECTRODES					
DENSITY, g/cc					
FROM UNAGED PASTE	1.42	1.44	1.43	1.40	1.38
FROM AGED PASTE (1)	-	-	1.47	1.45	-
COMPRESSIVE STRENGTH, Kg/cm ²					
FROM UNAGED PASTE	354	372	381	286	313
FROM AGED PASTE (1)	-	-	426	408	-

(1) 24 HR. AT 225°C.

Table 3

UPGRADING COAL TAR BINDERS BY ADDITION OF CARBON BLACK

PITCH	A		B	
	NONE	2.5%	NONE	2.5%
CARBON BLACK	NONE	2.5%	NONE	2.5%
SOFTENING POINT, °C	52	52	110	110
COKING VALUE, %	50	53	51	53
BENZENE INSOLUBLES, %	25	28	26	28
QUINOLINE INSOLUBLES, %	8	9	2	5
SODERBERG PASTE				
BINDER, %	30.5	38.5	30.5	32
ELONGATION, % (255°C)	78	32	88	59
BAKED ELECTRODES				
APPARENT DENSITY, g/cm ³	1.38	1.45	1.38	1.41
COMPRESSIVE STRENGTH, Kg/cm ²	295	434	274	388

Table 4

CONVERSION OF MANURE TO OIL BY HYDROTREATING

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INTRODUCTION

In an effort to utilize a significant potential energy source and at the same time reduce pollution, the Bureau of Mines has been experimentally converting organic wastes to oil. The original process (1,2) uses carbon monoxide and water to treat the organic material at temperatures of 350°-400°C and pressures near 4000 psi. Even though this reaction proceeds well and produces a good yield of oil, there are some technical problems that have to be resolved before the process would be economical. The major problems include the high operating pressure, the large amounts of energy necessary for heating the water reactant, and the purification of the process water containing organic solubles.

In our previous study (3) on bovine manure conversion, we reported that significant improvements in reducing operating pressure and energy requirement for heating were achieved by replacing large percentages of water with a suitable high boiling vehicle. It was also shown that synthesis gas can be used in place of carbon monoxide to convert manure to oil in reasonably good yield. The present work deals with further attempts to use manure-derived oil as a recycle vehicle in place of water. We have found that manure oil is an unsuitable vehicle, giving poor conversion and oil yield in the absence of a suitable catalyst. However, bovine manure, like coal, can be hydro-genated and liquefied at elevated temperatures and pressures in the presence of a vehicle and a cobalt molybdate catalyst. This process may be uneconomical because it requires fairly large amounts of expensive hydrogen in the reaction. A promising method for hydrotreating organic wastes using synthesis gas and a combination of cobalt molybdate-sodium carbonate catalyst is presented in this report. The proposed process requires no process water and results in the effective hydrogenation and deoxygenation of organic wastes without a significant consumption of hydrogen.

EXPERIMENTAL

The conversion of manure to oil was studied in a 500-ml magnetically-stirred, stainless steel autoclave. Bovine manure from Beltsville, Maryland, was used. Chemical analyses of two samples used are given in Table 1. A high boiling alkylnaphthalene-based oil (boiling above 235°C) and manure-derived oils were used as vehicles. A manure oil produced from the reaction of manure with CO and H₂O at 380° and 4500 psi was used as the starting vehicle. In several series of experiments using different gas reactants or catalytic conditions, each succeeding run within a series utilized the oil product recovered from the preceding run as the vehicle. The catalyst was a commercial cobalt molybdate supported on silica alumina used either in the presence or absence of sodium carbonate.

TABLE 1. Analyses of bovine manure (as used), percent

Sample	C	H	N	S	O (by diff.)	Ash	Moisture
1	44.2	6.2	2.5	0.35	39.9	6.9	3.8
2	42.5	5.7	2.3	0.35	34.7	14.5	4.2

For most of these experiments, hydrogen and synthesis gas (approximately equal parts of hydrogen and carbon monoxide) were used as gas reactants at initial pressures of 1000 to 1500 psi. Operating pressures ranged from 2000 to 3000 psi at reaction temperatures of 330° to 425°C, and the reaction was maintained for 15 to 60 minutes at the reaction temperature. After the experiment, rapid internal cooling of autoclave to ambient temperature was achieved. Total products were centrifuged at ambient temperature to obtain centrifuged liquid oils. Centrifuge 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 manure.

RESULTS AND DISCUSSION

Effects of Catalyst and Vehicle

The conversion of bovine manure to oil by reaction with synthesis gas is greatly influenced by the presence or absence of catalyst and vehicle. Initial experiments showed that bovine manure could be converted to oil by a mild hydrotreating with hydrogen or synthesis gas in the presence of alkylnaphthalene oil as vehicle. When a manure oil was used as vehicle, however, manure conversion and oil yield were poor, and the oil product became more viscous after each successive run. The use of sodium carbonate as catalyst (1) did not improve the oil quality. After being hydrotreated in the presence of a CoMo catalyst, manure oil became a good vehicle, and successive runs using the manure oil product as vehicle in the presence of CoMo catalyst gave good results. The fluidity of vehicle oil could be maintained throughout many successive runs, suggesting the feasibility of using manure oil product as a recycling vehicle. Analyses of vehicles are given in Table 2. Note that properties of manure oil are improved after hydrotreating with either hydrogen or synthesis gas in the presence of a CoMo catalyst. The oxygen content and oil viscosity are reduced. Effects of vehicle and catalyst on the conversion of manure to oil by hydrotreating with synthesis gas are shown in Table 3. At temperatures of 380° and 425°C and an operating pressure of about 3000 psi, both alkylnaphthalene oil and manure oil used as vehicle gave high conversion and good oil yield when the CoMo catalyst was present.

TABLE 2. Analyses of vehicles, percent

	C	H	N	S	O (by diff.)	Kinematic viscosity, centistoke at 60°C
Alkylnaphthalene oil	90.6	8.7	0.06	0.37	0.3	1.7
Manure oil ^a	80.7	9.6	4.0	0.20	5.5	550
Treated manure oil ^b	80.9	10.3	4.5	0.21	4.1	120
Treated manure oil ^c	83.8	10.2	4.6	0.11	1.3	17

^a Prepared by reaction of manure with CO and H₂O at 380°C and 4500 psi.

^b Manure oil was hydrogenated with H₂ at 380°C and 2200 psi in the presence of a CoMo catalyst.

^c Manure oil was hydrotreated with synthesis gas at 425°C and 2600 psi in the presence of a CoMo catalyst.

TABLE 3. Effects of vehicle and catalyst on conversion of manure

(vehicle:manure = 2.3:1, 1500 psi initial synthesis gas pressure)

Vehicle	Alkylnaphthalene oil				Manure oil	
Temperature, °C	380	380	425	425	380	425
Catalyst ^a	-	CoMo	-	CoMo	CoMo	CoMo
Operating pressure, psi	3200	3000	3200	3100	3000	3000
Time, min.	30	30	15	15	30	15
Conversion, percent ^b	86	92	88	95	93	93
Oil yield, percent ^b	34	47	35	45	45	40

^a Two parts catalyst per 100 parts feed of manure plus vehicle.^b Weight percent of maf manure.Effects of Gas Reactants

To determine the effects of various gas reactants on the conversion of manure, hydrogen, carbon monoxide, and synthesis gas were compared. Vehicle oils for different runs were conditioned by pretreating with the different gases at desired experimental conditions. At an initial pressure of 1500 psi, operating pressures at 380°C reaction temperature ranged from 2600 to 3500 psi, depending on the extent of hydrogen consumption or hydrogen formation during the reaction. Data are given in Table 4.

Experiments with hydrogen indicate that cobalt molybdate catalyzes the hydrogenation reaction under the operating conditions. The conversion, oil yield, and hydrogen consumption were increased by the use of the catalyst. When carbon monoxide or carbon monoxide and water were used to react with manure, both conversion and oil yield were low, and the oil product behaved poorly as a vehicle. But synthesis gas could be used in place of hydrogen without adverse effects on manure conversion, oil yield, and oil quality. In this comparison, hydrogen consumption decreased from 3.0 to 2.3 percent, water yield decreased from about 23 to 13 percent, but carbon dioxide formation increased considerably. The oxygen content in manure was removed in the form of water and carbon dioxide in both cases.

TABLE 4. Effects of gas reactants on conversion^a

(manure oil:manure = 2.3:1, 30 minutes at 380°C)

Gas reactant	H ₂		CO		H ₂ + CO (1:1)	
Catalyst ^b	-	CoMo	-	CoMo	-	CoMo
Initial pressure, psi	1500	1500	1500	1000 ^c	1500	1500
Operating pressure, psi	2900	2700	3500	2900	3200	3000
Conversion, percent	78	97	72	84	81	93
Oil yield, percent	23	47	19	34	23	45
H ₂ consumption, percent	2.2	3.0	(1.2) ^d	(1.6) ^d	1.4	2.3
CO ₂ formation, percent	17	16	78	86	60	42

^a Data are given in weight percent of maf manure.^b Two parts of catalyst per 100 parts feed of manure plus manure oil.^c Water (33 parts per 100 parts manure) was also added as the reactant.^d Hydrogen formation.

Effects of Reaction Variables

Pressure. The effect of operating pressure on the conversion of manure was studied for both hydrogen and synthesis gas. The reactions were carried out at 380°C for 30 minutes. Starting at the same initial pressures, the hydrogen runs did not reach as high operating pressures as the synthesis gas runs, probably because of the greater hydrogen consumption. As shown in Figure 1, the conversion and the oil yield increase slightly with pressure in the range of 1500 to 3000 psi, but there are very little differences between hydrogen and synthesis gas.

Temperature. Of all the variables investigated, temperature has the most dramatic effect on the properties of the oil product. Experiments were conducted at an initial pressure of 1500 psi but at different operating pressures, ranging from 2600 to 3100 psi, depending on the reaction temperature and gas reactant. The reaction was maintained for different periods at different temperatures: 60 minutes at 330°C, 30 minutes at 380°C, and 15 minutes at 425°C. The results in Table 5 indicate, for both hydrogen and synthesis gas runs, that the hydrogen consumption increased with temperature without improvements in the conversion or oil yield. However, significant improvements in oil product quality were observed with increasing temperature; carbon content increased, oxygen content decreased, and viscosity was reduced. The change in the properties of oil product is accompanied by some decrease in the oil yield, mainly because the oxygen-containing groups are further reduced and the product oil is subjected to cracking. The amount of low molecular weight hydrocarbon gases produced was small but increased with temperature. Again, in comparison with the hydrogen runs, the synthesis gas runs yielded greater amounts of carbon dioxide but smaller amounts of water. In the hydrogen runs, the constant amount of carbon dioxide formed (average 16 percent) is probably all that could be produced from the thermal decomposition of the manure.

TABLE 5. Hydrotreating of manure at various temperatures^a

(manure oil:manure = 2.3:1, CoMo catalyst, 1500 psi initial pressure)

	H ₂			H ₂ + CO (1:1)		
	330	380	425	330	380	425
Temperature, °C	330	380	425	330	380	425
Operating pressure, psi	2600	2700	2700	3100	3000	3000
Time, minutes	60	30	15	60	30	15
Conversion, percent	95	97	94	94	93	93
Oil yield, percent	49	47	39	47	45	40
CH ₄ formation, percent	0.3	0.9	2.7	0.5	1.3	3.5
CO ₂ formation, percent	17	16	16	31	42	47
H ₂ O yield, ^b percent	20	23	25	16	13	10
H ₂ consumption, percent	2.3	3.0	4.5	2.0	2.3	2.6
Oil analysis, percent						
C		81.9		77.5	81.5	83.4
H		9.7		9.8	9.9	10.2
N		4.2		4.3	4.4	4.6
S		0.18		0.19	0.10	0.11
O (by diff.)		4.0		8.2	4.1	1.7
Kinematic viscosity of oil at 60°C, centistoke		118		563	129	17

^a Data are given in weight percent of maf manure.

^b Excluding moisture content in manure.

Reaction Time. Figure 2 shows the effect of time on the conversion of manure by hydrogen at 380°C. The time required to reach 380°C in the autoclave was about 60 minutes, and the reaction was then maintained at this temperature from 0 to 60 minutes. Nearly 85 percent of conversion occurred before the system reached 380°C, and the conversion approached a limit of about 97 percent after the reaction was in progress at 380°C for 30 minutes. All carbon dioxide was produced before the reaction mixture reached 380°C (before zero time). The progress of the hydrogenation, and probably the upgrading of the oil properties, can be better measured by the hydrogen consumption which increased from 1.4 percent at zero time to 3.6 percent at 60 minutes.

Effect of Sodium Carbonate

Two comparative series of experiments were carried out hydrotreating bovine manure. In the first series, manure was hydrotreated with synthesis gas at an initial pressure of 1000 psi and 380°C reaction temperature for 30 minutes in the presence of a CoMo catalyst and a manure oil vehicle. Various amounts of water (0 to 50 parts per 100 parts of manure) were added in different runs to determine the effect of moisture content of manure. In each succeeding run, the oil product recovered from the preceding run was used as vehicle. In the second series, experiments were carried out in the similar manner except that 2 percent Na₂CO₃ (based on feed of manure plus vehicle) was added in addition to the CoMo catalyst.

Results are shown in Table 6. Operating pressures were higher in Series 2 than in Series 1 at equal water levels. The average oil yield in the presence of Na₂CO₃ increased and the kinematic viscosity of the product decreased. In addition, hydrogen consumption was reduced as shown in Figure 3. Less hydrogen was consumed with increasing moisture content of manure, without any effect on the conversion of manure to oil. Other noticeable effects of the Na₂CO₃ addition were increased carbon dioxide formation and decreased water yield. It is apparent that in the presence of Na₂CO₃, hydrogen consumed is partly replenished by the reaction of carbon monoxide with water during hydrotreating. As a result, effective hydrogenation and deoxygenation of manure are accomplished without significant consumption of hydrogen.

CONCLUSIONS

Bovine manure is hydrogenated and liquefied by hydrogen or synthesis gas (equal amounts of hydrogen and carbon monoxide) at temperatures of 330° to 425°C and operating pressures of 1500 to 3000 psi in the presence of a recycle manure oil and a cobalt molybdate catalyst. With an increase in temperature, oxygen content and viscosity of oil product decrease, but hydrogen consumption increases. Synthesis gas can be used in place of hydrogen to reduce hydrogen consumption without adverse effects. A significant improvement on this process, when using synthesis gas, is achieved by adding sodium carbonate to the reaction mixture; hydrogen consumption is reduced markedly, oil yield improved, and oil viscosity reduced. Manure with moisture contents up to about 35 weight percent was evaluated and found acceptable as feedstocks. The other feature of the process is that it requires no process water, and this eliminates the problem of heating or purifying large amounts of the process water.

REFERENCES

1. H. R. Appell, Y. C. Fu, S. Friedman, P. M. Yavorsky, and I. Wender. BuMines RI 7560, 1971, 5 pp.; Agr. Eng., March 1972, pp. 17-19.
2. S. Friedman, H. H. Ginsberg, I. Wender, and P. M. Yavorsky. Third Mineral Wastes Utilization Symp., IIT, March 1972.
3. Y. C. Fu, S. J. Metlin, E. G. Illig, and I. Wender. Preprints, Div. Fuel Chem., Am. Chem. Soc., vol. 17, No. 1, 37 (1972).

TABLE 6. Effect of Na₂CO₃ on hydrotreating of bovine manure by synthesis gas
 (manure oil:manure:water = 2.3:1:0-0.5, 1000 psi initial pressure, 380°C, 30 minutes)

Series	Catalyst	Operating pressure, ^a psi	Conversion, percent	Oil		H ₂ consumption, percent	CO ₂ formation, percent	Kinematic viscosity, ^b cs at 60°C
				yield, percent	42-44 46-48			
1	CoMo	2100-2700	95-98	42-44		1.0-2.1	34-45	138
2	CoMo-Na ₂ CO ₃	2200-3000	95-98	46-48		(0.75) ^c -0.4	67-86	65

^a Operating pressure increased with the amount of water added.

^b Kinematic viscosity of the oil product obtained at the end of the series.

^c Hydrogen formation.

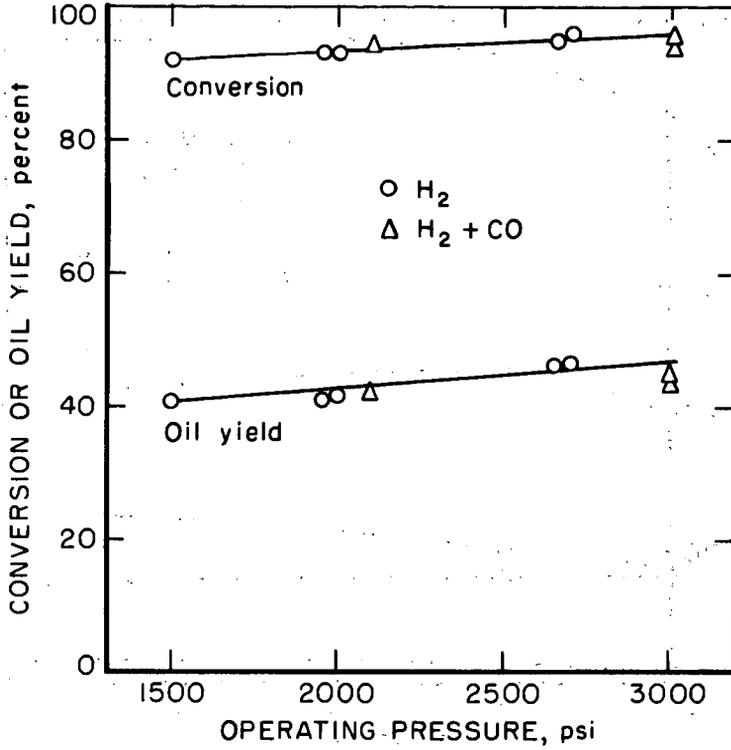


Figure 1- Effect of operating pressure on conversion of manure at 380°C

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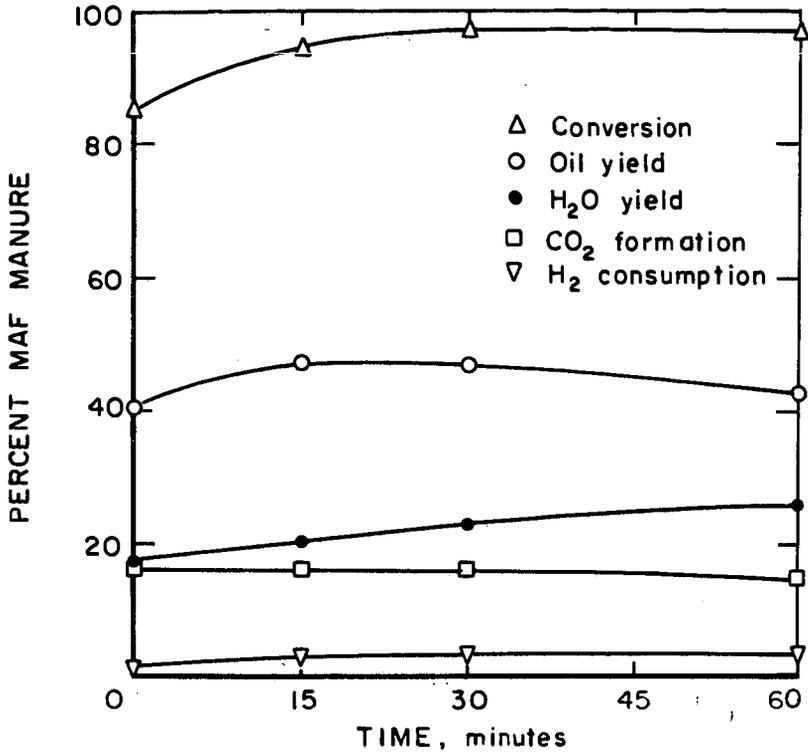


Figure 2-Effect of time on conversion of manure by H_2 at $380^\circ C$.

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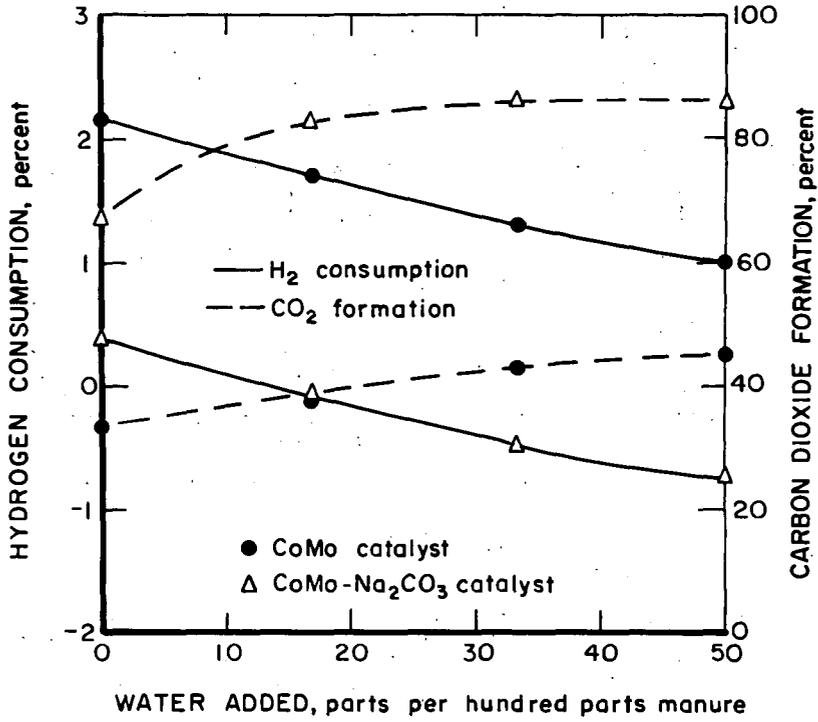


Figure 3—Effect of moisture content of manure at 380°C.