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Pressure Carboxylation of Lignitic Minerals with Carbon Dioxide

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PRESSURE CARBOXYLATION OF LIGNITIC MINERALS
WITH CARBON DIOXIDE

by

Kishore P. Jhamvar

B. Chem. Eng., University of Bombay, India 1965

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Submitted to the Faculty

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This thesis submitted by Kishore P. Jhamvar in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

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Title Pressure Carboxylation of Lignitic Minerals with Carbon Dioxide

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Degree Master of Science

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ABSTRACT

Leonardite and lignite were carboxylated by the Kolbe-Schmitt reaction in order to increase the acidity and hence the cation exchange capacity. A larger carboxyl group content would increase solubility and effectiveness in commercial application such as a thinner for oil-well drilling fluids.

The carboxylation was performed in a heated autoclave under a high carbon dioxide pressure. The Kolbe-Schmitt reaction was used in an anhydrous medium and in a slurry medium and in a modification developed by Marasse using anhydrous potassium carbonate. The reaction material consisted of moisture free, fine powdered potassium salts of leonardite and lignite. Temperature was varied from 100°C to 180°C and the initial carbon dioxide pressure from 225 psig to 900 psig. The time of reaction was also varied between 4 and 24 hours. The extent of reaction was evaluated from changes in total acidity, hydroxyl acidity and carboxyl acidity of the treated material.

The maximum increase obtained in carboxyl acidity was 39 per cent and that in total acidity was 89 per cent of the increase predicted on the basis of complete ortho substitution to all existing hydroxyl groups.

The optimum conditions found were at 150°C temperature and a pressure of 1060 psig for 8 hours.

INTRODUCTION

High humic acid content and presence of functional groups suggest a variety of non-fuel uses for the naturally occurring oxidized lignite known as leonardite. One of the major commercial uses of leonardite is as an additive for control of viscosity in oil well drilling fluids. Coals having high total ion-exchange capacities and a fixed carbon to volatile matter ratio of less than one were found to be good thinning agents (23). Increasing the acidity and hence the total cation exchange capacity would make leonardite more effective in these applications.

The objective of this research was to increase the acidity of leonardite and lignite by chemical treatment. The investigation was designed to develop the optimum conditions required for carboxylation of leonardite to increase the acidity.

The approach to this problem was to substitute carbon dioxide directly into the coal molecule, such as in the Kolbe-Schmitt reaction and its modification by Marasse (16). The carboxylation was carried out under elevated pressures in heated autoclave between gaseous carbon dioxide and finely powdered alkali salts of humic acids of leonardite. In the Marasse modification the potassium salts of humic acids were

mixed with anhydrous potassium carbonate and then the carboxylation was carried out under carbon dioxide pressure. The extent of the reaction was evaluated from changes in total acidity, hydroxyl acidity and carboxyl acidity of the leonardite.

BACKGROUND

The Lignitic Minerals

The Western part of North Dakota has huge reserves of lignite coal, and found in association with lignite are smaller deposits of naturally oxidized lignite known as leonardite. Leonardite is a coal-like substance, somewhat similar in structure and composition to lignite but significantly different from lignite in its oxygen content. Leonardite is believed to be weathered lignite formed by the action of oxygen in alkaline ground waters. Leonardite is rich in humic acids, containing up to 86 per cent humic acids on the moisture and ash free basis (28).

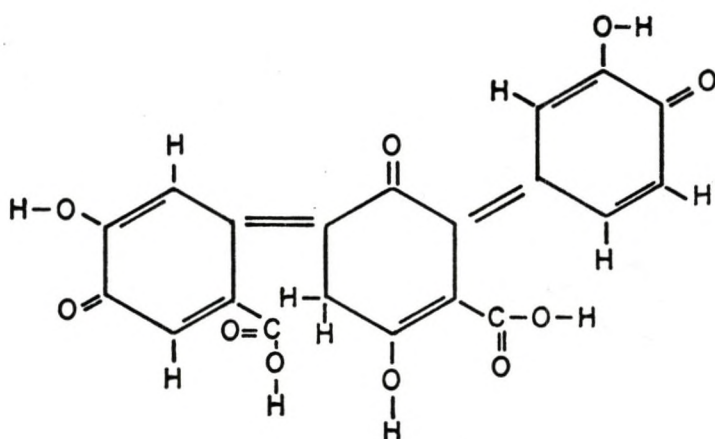
Humic acids are closely related hydroxy-carboxylic aromatic compounds. These are mostly present in leonardite as insoluble salts of calcium (29). Abbott (1) describes humic acids as those humus substances that contain ionizable hydrogen and give typical salts with strong bases. Physically, humic acids are dark brown to black in color, and are amorphous and non-volatile substances. The alkali solubility of humic acids is due to carboxyl and phenolic hydroxyl groups. Fowkes and Frost (13) report a typical functional group analysis of leonardite and lignite which is shown in Table 1.

TABLE 1

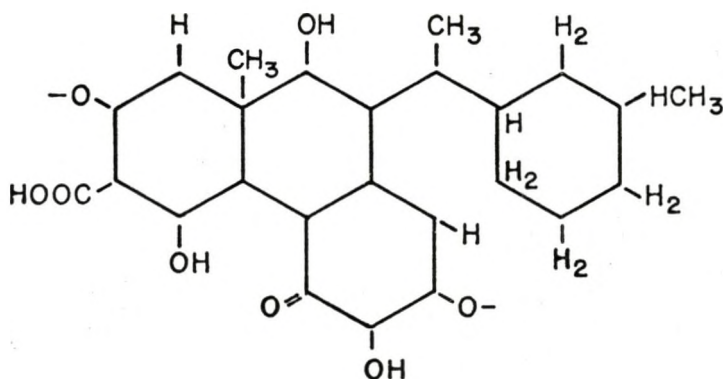
TYPICAL FUNCTIONAL GROUP ANALYSIS OF LIGNITIC MATERIALS (MAF BASIS)

	Total per cent	Oxygen in functional groups, weight per cent					Non- reactive	Total
		C	COOH	OH	CO	OCH ₃		
Lignite	73.8	9.2	4.8	4.3	0.5	1.1	19.9	
Leonardite	63.9	17.4	4.8	4.3	0.5	1.5	28.4	

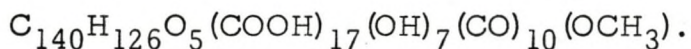
Scientists have not yet succeeded in formulating a universally accepted definition of humic acids. Yet it is a fact that the humic acids have a typical characteristic pattern or stable structure whose properties are determined chiefly by certain active groups; particularly phenolic hydroxyl and carboxyl groups (2). Gillet (3) proposed a structural formula of humic acids.



Clem (6) describes another possible structural formula for humic acids.



Fowkes and Frost (14) have calculated the following formula for leonardite from the elemental and functional group analysis.



Leonardite has a potential as a source of organic chemicals. It is used as a stabilizer for ion-exchange resins in water treatment (15). Recently leonardite has been proposed as binding material for taconite pellets (12). Leonardite is used as a soil conditioner, as a dispersant and for viscosity control in oil well drilling fluids (21).

Leonardite As A Thinning Agent

One of the most common oil well drilling fluid control agents is known as quebracho, a water soluble tannin extract of the quebracho trees. It is obtained from Argentina. Odenbaugh and Ellman (22) report that the leonardite is the most satisfactory of 70 naturally occurring and synthetic available substitutes for quebracho. In 1965, more than 23,600 tons of quebracho worth 3.4 million dollars were used in drilling muds in United States.

Odenbaugh and Ellman (22) report that an estimated one-third of the total production of leonardite is ultimately used as oil well drilling fluid additives. Based on total production figures for 1964-66, this means that approximately 60,000 tons of leonardite having an as-mined value of about 120,000 dollars were used by the petroleum industry annually. Thus the amount of leonardite used by the petroleum industry

exceeds that of quebracho. Also the cost of leonardite is only \$2.00 per ton as compared to the cost of about \$144.00 per ton for quebracho. This indicates that increased use of leonardite could result in large savings.

Leonardite as a result of its ion exchange capacity performs a very useful function in changing the properties of drilling muds. It reduces viscosity, lowers gel strength and fluid loss and is a good emulsifier (4). A brief review of the nature of a drilling fluid and how its properties are controlled follows to clarify the use of leonardite in drilling fluid.

The drilling operation requires a liquid medium to cool the drill bearings and to flush away sand, chips and other cuttings. Water is the cheapest and most readily available liquid medium but its use is limited to depths of 2500-3500 feet. Also as a result of low viscosity of water and force of gravity a point is reached where cuttings cannot be flushed from the drilling hole.

The chip-carrying capacity of water can be increased by addition of a thickening material such as bentonite clay. Bentonite gives a lubricating action and has a wall-building characteristic but it has certain limitations also. The strong gelling action of bentonite helps in keeping the cuttings in suspension when the drilling operation is stopped temporarily. This suspension when fed into a piston-type pump for reinjection into the well tends to score the cylinder walls,

shortening the life of the pump (5).

Bentonite in drilling fluid also helps to control fluid loss. During the drilling operation, the pressure forces the water out of the mud, depositing a cake on the inside of the hole. The cake continues to grow in thickness resulting in a larger torque necessary to overcome the resistance while drilling, and choking ultimately occurs. The Wyoming-type bentonite has a high content of colloidal fines and deposits a thin, tough cake on the walls of the hole resulting in a minimum loss of fluid to the formation.

The strong gelling action of bentonite, however, has its drawbacks. Clem (5) reports that one per cent increase in the addition of bentonite doubles the gelling action. This necessitates the addition of a powerful thinner which disperses and does not harm the bentonite in other functions.

Leonardite, through its hydroxyl and carboxyl groups, forms water soluble salts with sodium, potassium, ammonium and lithium. The hydrophilic portion of the alkali salt gives dispersibility in water, permitting emulsification. According to Rogers (26) the mechanism by which the water soluble salts of leonardite function is as follows.

The structure of the bentonite particles is a three-layer sheet with the top and bottom layers of silicate and the central layer of aluminum oxide plus hydroxyl groups (25). The layers stretch continuously in two directions until broken where the unsatisfied

charges get exposed. When the particles assume equilibrium positions with respect to each other the gel structure develops. The attractive and repulsive edge charges of different sheets cement the mass together. The like charges on surfaces of the particles prevent agglomeration and add to the strength of the structure. Thinning agents become absorbed on the exposed edges reducing edge-face attraction and allowing face to face orientation. This improvement in laminar structure results in better resistance to permeation and the drilling fluid has then lower fluid loss (6).

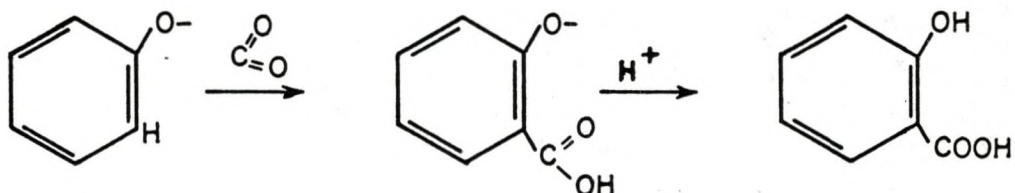
Chemical modification in the structure of leonardite in terms of increased total ion-exchange capacity and its water solubility could increase its effectiveness over a wider range of composition of drilling muds and with respect to other thinners such as quebracho (7).

The Kolbe-Schmitt Reaction

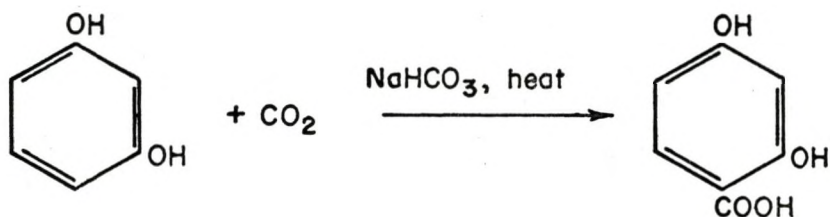
The Kolbe-Schmitt reaction has been a standard procedure for the preparation of aromatic hydroxy acids for over ninety years. Generally, substitution occurs ortho to the phenolic hydroxyl group, but cases of para substitution are also known (17).

The most important commercial application of the Kolbe-Schmitt reaction is that of preparation of salicylic acid from phenol. A solution of phenol in aqueous alkali is evaporated to dry powder. The sodium phenolate is pressurized under carbon dioxide to 4-7 atmospheres and

heated to 125°C . Acidification gives nearly theoretical yields of free acid (10).



There are several factors which influence the Kolbe-Schmitt reaction. The presence of moisture has been known to prevent initial addition of carbon dioxide (19). The more reactive di- and trihydric phenols require milder conditions for carboxylation. For example, β -resorcylic acid can be prepared in 60 per cent yield by the carboxylation of resorcinol in sodium bicarbonate solution (18).



In this respect, humic acids of leonardite are polyhydroxy compounds and may respond to the carboxylation in slurry form.

At a given temperature, increase in pressure above a certain minimum value does not greatly affect the course of the carboxylation

reaction (20). In certain cases pressures as high as 130 atmospheres have been used. The reaction time is also varied considerably. Some reactions have been carried out for 24 hours. The temperature is known to influence the reactivity of the reacting material as well as the position of substitution.

In 1893, Marasse introduced a simple modification of the Kolbe-Schmitt reaction. He mixed free phenol with an excess of anhydrous potassium carbonate and carboxylated under carbon dioxide pressure and at elevated temperatures to obtain the potassium salt of salicylic acid. It has been observed that in certain cases the Marasse modification gives better yields than the Kolbe-Schmitt reaction (18).

EXPERIMENTAL PROCEDURE

A 25 gram sample of leonardite or lignite was weighed on an analytical balance and transferred carefully to a beaker containing 375 milliliters of standard 2 per cent potassium hydroxide solution and stirred. Stirring was continued until all the solid was dispersed. The analysis of the leonardite and lignite samples used for the experiments is given in Appendix D.

The slurry was evaporated to dryness on a steam bath. The dried powder was crushed between rolls to pass a 20 mesh screen, then dried in an oven at 105^oC. The moisture free material was cooled and weighed and transferred to a steel liner which fitted closely inside a one-liter autoclave, Parr series 4500. The autoclave was sealed and then flushed twice by pressurizing with carbon dioxide to 200 psig and releasing, and finally pressurized with "bone-dry" carbon dioxide to 600 psig. Great care was taken to keep the reaction material free of moisture. The autoclave was heated to the desired temperature in about 40 to 50 minutes. The temperature was maintained constant by circulating cooling water through the cooling coil and around stirrer packing glands. The reaction was continued for 8 hours.

The temperature was controlled by a very careful manual

adjustment of electrical heat input and heat removal by cooling water circulation. With experience, the operator was able to hold the desired temperatures with an accuracy of $\pm 2^{\circ}\text{C}$.

The autoclave was cooled overnight. The product was removed from the steel liner to a watch glass and dried in an oven at 105°C . After cooling in a desiccator two samples were weighed accurately and analyzed for acidities.

In the experiments using the Marasse modification about 14 grams of anhydrous potassium carbonate were thoroughly mixed with the reaction material in the liner just before sealing the autoclave.

ANALYTICAL PROCEDURE

The analytical procedure developed by Purandare (24) is largely based on the analysis performed by Ubaldini (27). The procedure reported by Purandare has been followed as a standard procedure with only slight modifications.

A sample of carboxylated product was treated with small amount of distilled water and stirred until dispersion was complete. The solution was centrifuged to remove undissolved and suspended material. The clear liquid in the centrifuge tube was decanted into a beaker. The residue remaining in the centrifuge tube was washed with distilled water and again centrifuged and decanted. Washings were added to the solution in the beaker. The washing and centrifuging operation was repeated until the washings were observed to be colorless, indicating complete extraction of humic acids from the sample. The extract was concentrated by evaporation to about 50-75 milliliter total volume over a steam bath, and after cooling acidified with concentrated hydrochloric acid to a pH of 4. This precipitated the humic acids. Precautions were taken not to add excess hydrochloric acid which, otherwise, would cause peptization in later filtration. The humic acid precipitate was then completely dried in a beaker heated by a hemispherical heating mantle.

The humic acid precipitate was washed with very dilute hydrochloric acid to remove any alkali chlorides formed as a result of the reaction between hydrochloric acid and alkali salt of humic acid and potassium carbonate. Distilled water could not be used because repeated washings with distilled water causes redispersion of humic acids. The tared filter paper containing humic acids was dried in an oven at 105°C for more than one hour to remove all moisture, then cooled and weighed. The yield of humic acids was then calculated.

Usually the total acidity of humic acids can be determined by treatment with an aqueous solution of standard alkali and then back-titrating the excess alkali with standard hydrochloric acid. This method, however, could not be used on the product from leonardite carboxylation because of the fact that the colloidal dispersion of leonardite in alkali could not be filtered and the end point of titration was not clear.

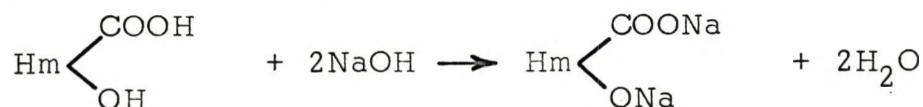
The following procedure was adopted to overcome these difficulties. The filter paper with humic acids was transferred to a 500 milliliter round bottomed flask and 50 milliliter of $\frac{N}{5}$ alcoholic sodium hydroxide solution was added. The suspension was refluxed on a heating jacket for 30 minutes. A water condenser was provided so that no alcohol escaped during refluxing. The sodium humate formed was insoluble in alcohol and precipitated. The flask was allowed to cool and the suspension filtered. The filtrate was stored in a 250 milliliter

erlenmeyer flask. A 10 milliliter aliquot portion of this filtrate was titrated in duplicate against 0.1 N hydrochloric acid. This gave the total acidity (carboxyl and hydroxyl).

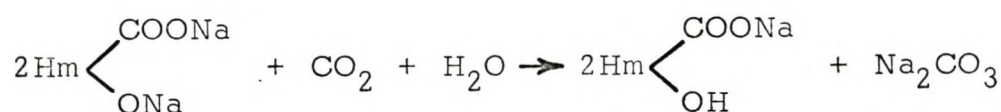
A flow sheet explaining the steps involved in the analysis is shown in Figure 1.

The filter paper with the residue after filtration was transferred to the original round bottomed flask and 100 milliliter of 75 per cent ethanol solution was added to it. Carbon dioxide was then bubbled through the slurry for about 45 minutes. The slurry was filtered and an aliquot portion titrated to pH 7.0 with 0.1 N hydrochloric acid using a pH meter to determine the end point. This titration gave equivalents of hydroxyl acidity in the sample.

By subtracting hydroxyl acidity from the total acidity, the carboxyl acidity in a given sample of leonardite was obtained. The reaction in the first part of the analytical procedure could be explained as follows (Hm represents basic humate):



When carbon dioxide is passed through the slurry following reaction takes place:



This reaction represents the hydroxyl acid content of the humic acids.

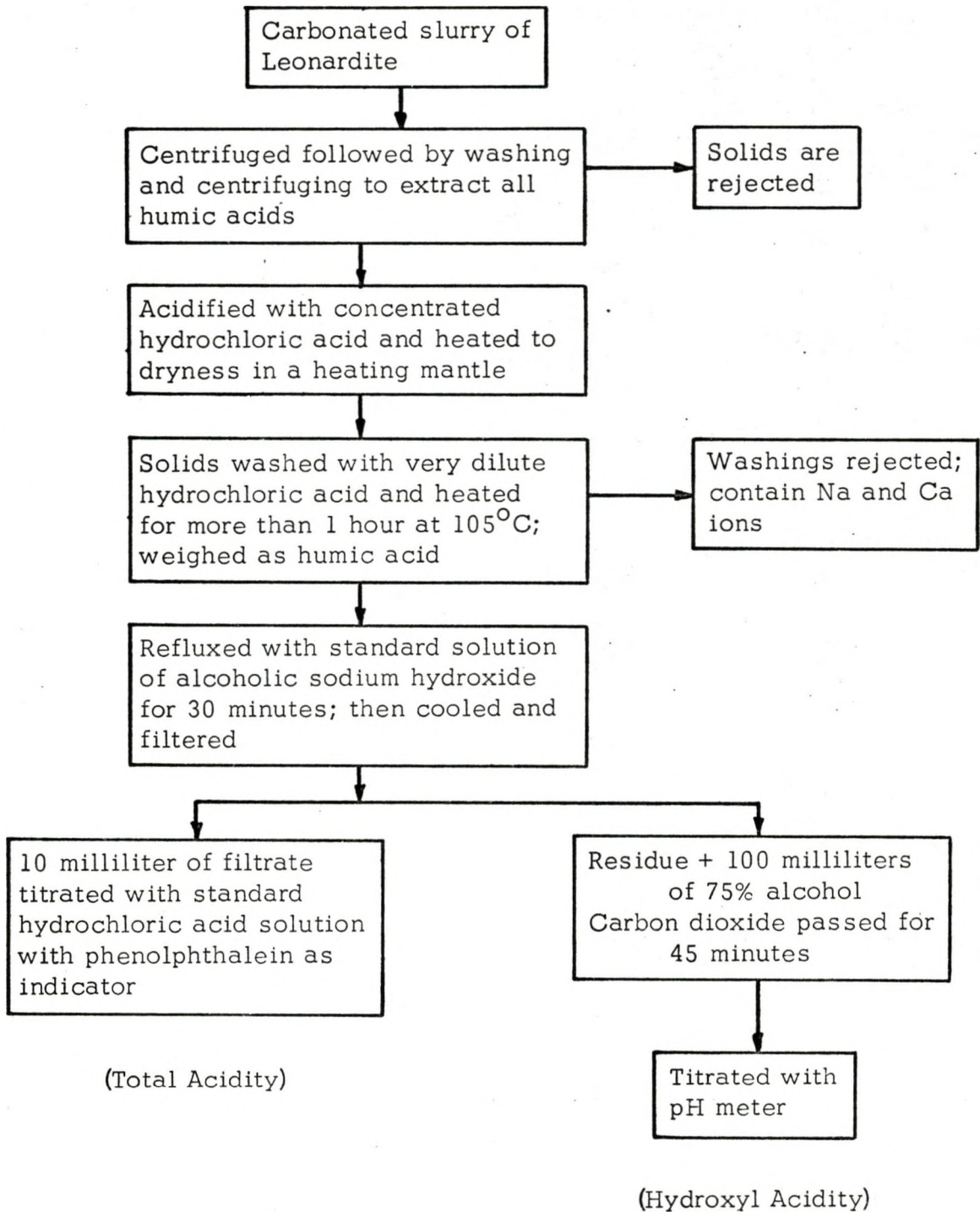


Fig. 1.--Flow Sheet for Analysis.

EXPERIMENTAL RESULTS

Fifteen carboxylation runs were carried out in all. Three methods of carboxylation were tried: the Kolbe-Schmitt reaction in anhydrous form, the Kolbe-Schmitt reaction in slurry form and the Marasse modification using anhydrous potassium carbonate. The temperature was varied from 100°C to 180°C and the initial pressure of carbon dioxide from 225 psig to 900 psig.

The results of the experiments with leonardite and lignite are shown in Tables 2 and 3 respectively. Average per cent yield of humic acids and average acidities in milliequivalents of acid per gram of raw material (MAF) are tabulated for duplicate determinations on each run. Complete analytical results are presented in Appendix E. A detailed sample calculation has been shown in Appendix B.

Figure 2 shows the plot of total acidity in terms of milliequivalents of acid per gram of leonardite (MAF) against temperature for the Kolbe-Schmitt reaction in anhydrous form and the Marasse modification using anhydrous potassium carbonate. The temperature was varied from 120°C to 180°C while the initial carbon dioxide pressure was 600 psig and the time of reaction was 8 hours. In Figure 3 carboxyl acidity as milliequivalents of acid per gram of leonardite (MAF) is plotted against

temperature for the Kolbe-Schmitt reaction in anhydrous form and the Marasse modification.

The reproducibility of the experiments was investigated by duplicating a run. Experiment 4 is the duplicate of experiment 3, and the duplicate experiments agreed within 2.5 per cent in total acidity measurements.

TABLE 2

RESULTS OF EXPERIMENTS WITH LEONARDITE

Acidities in milliequivalents of acid per gram of leonardite (MAF)
and yield of humic acid as per cent per gram of leonardite (MAF)

Raw leonardite:

Carboxyl acidity	5.94
Hydroxyl acidity	4.14
Total acidity	10.08
% Yield of humic acids	77.7%

20

Carboxylated products:

A) The Kolbe-Schmitt reaction in anhydrous form

Expt. no.	Initial CO ₂ pressure	Temp.	Reaction pressure	Time	Total acidity	Carboxyl acidity	Hydroxyl acidity	Yield of humic acids
	psig	°C	psig	hrs.				per cent
1	225	100	295	4	10.00	5.70	4.30	78.5
2	600	120	920	8	11.53	7.04	4.48	77.9

TABLE 2--Continued

Expt. no.	Initial CO ₂ pressure	Temp.	Reaction pressure	Time	Total acidity	Carboxyl acidity	Hydroxyl acidity	Yield of humic acids
	psig	°C	psig	hrs.				per cent
3	600	150	1040	8	11.05	6.32	4.79	77.7
4	620	150	1000	8	10.80	6.09	4.71	78.3
5	600	180	1130	8	11.35	6.37	4.98	79.9
6	800	150	1070	24	10.78	6.27	4.50	79.5
7	900	150	1710	8	9.01	5.48	3.53	74.1

21

B) The Kolbe-Schmitt reaction in slurry form

8	600	150	960	8	8.40	5.16	3.24	74.2
9	600	150	960	8	8.84	6.03	2.82	70.4
10	600	180	1020	8	7.55	4.72	2.83	67.7

C) The Marasse modification using anhydrous potassium carbonate

11	600	120	930	8	13.46	7.42	6.04	75.7
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TABLE 2--Continued

Expt. no.	Initial CO ₂ pressure	Temp.	Reaction pressure	Time	Total acidity	Carboxyl acidity	Hydroxyl acidity	Yield of humic acids
	psig	°C	psig	hrs.				per cent
12	600	150	1060	8	13.74	7.57	6.17	90.4
13	600	180	1120	8	13.37	7.33	6.05	79.4

TABLE 3

RESULTS OF EXPERIMENTS WITH LIGNITE

Acidities in milliequivalents of acid per gram of lignite (MAF)
and yield of humic acids as per cent per gram of lignite (MAF)

Raw lignite:

Carboxyl acidity	2.74
Hydroxyl acidity	4.01
Total acidity	6.75
% Yield of humic acids	12.8%

23

Carboxylated products:

A) The Kolbe-Schmitt reaction in anhydrous form

Expt.	Initial CO ₂ pressure	Temp.	Reaction pressure	Time	Total acidity	Carboxyl acidity	Hydroxyl acidity	Yield of humic acids
	psig	°C	psig	hrs.				per cent
14	615	150	1000	8	6.82	2.54	4.28	10.6
15	700	150	1240	8	6.87	3.12	3.75	28.6

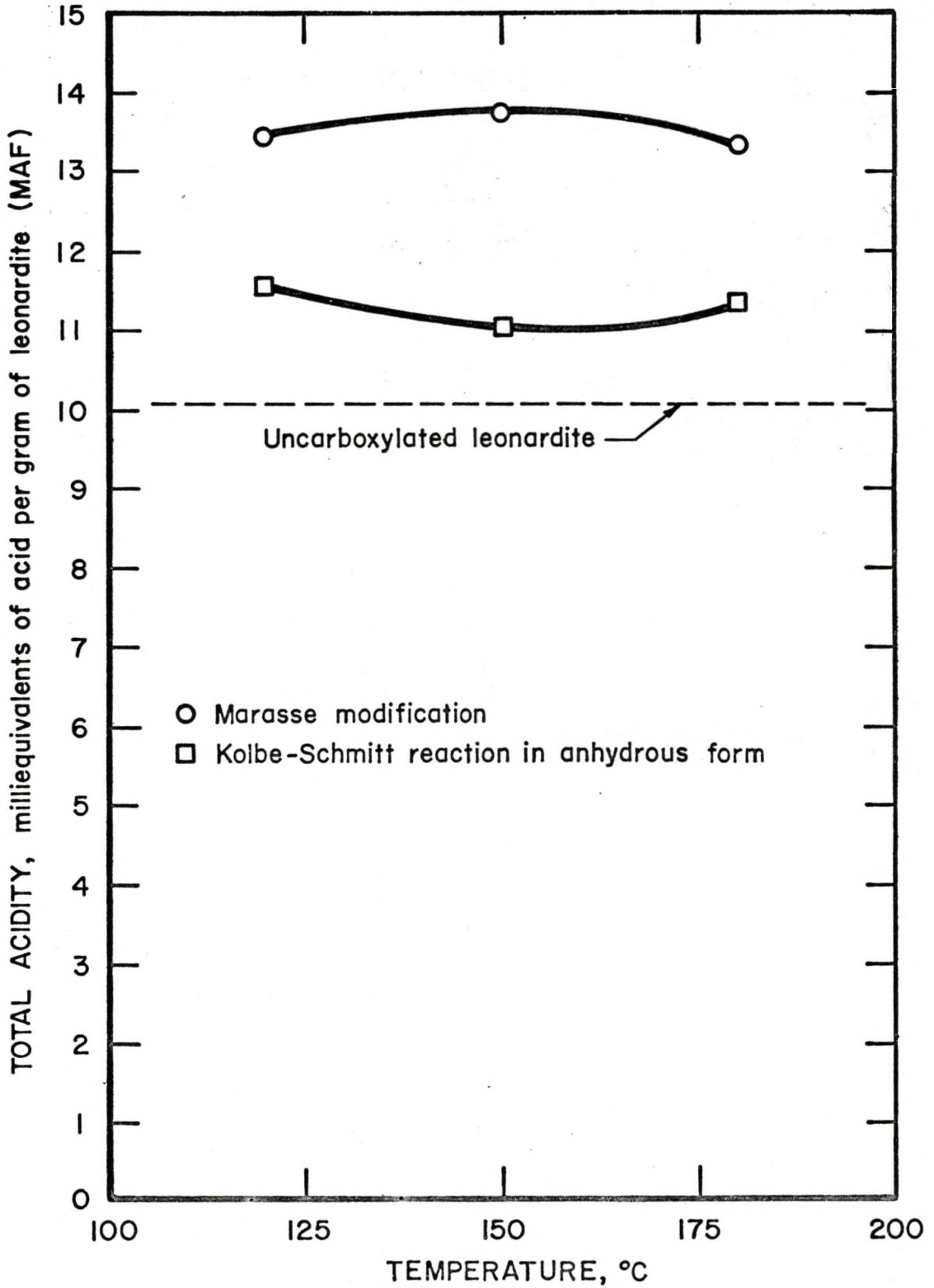


Figure 2 Total acidity in terms milliequivalents of acid per gram of leonardite (MAF) against temperature.

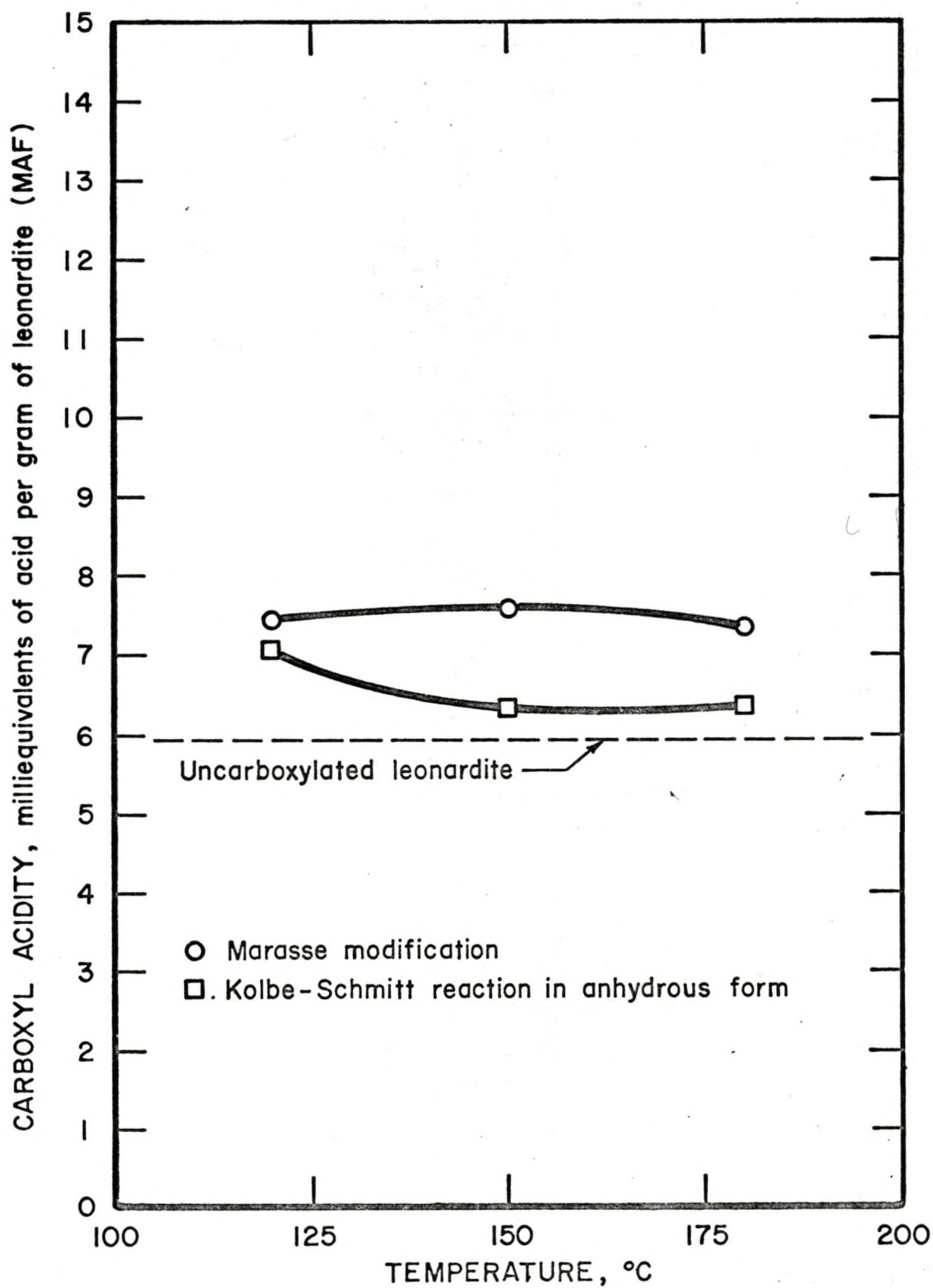


Figure 3 Carboxyl acidity in terms of milliequivalents of acid per gram of leonardite (MAF) against temperature.

DISCUSSION OF RESULTS

In the Kolbe-Schmitt reaction with monohydric phenolic compounds the hydroxyl group directs the substitution of one carboxyl group in the ortho or para position. In the absence of definite knowledge of structure of humic acids of leonardite and lignite, it was assumed that each hydroxyl group would substitute one carboxyl group on the coal molecule. Hence the maximum possible increase in carboxyl acidity would be equal to the initial hydroxyl acidity, which for the sample tested was 4.14 milliequivalents of acid per gram of leonardite (MAF). The greatest increase in carboxyl content obtained was from 5.94 to 7.57 milliequivalents of acid per gram of leonardite (MAF). Thus the maximum increase in carboxyl acidity was 1.63 milliequivalents of acid per gram of leonardite (MAF) or 39 per cent of maximum expected increase. The total acidity increased by 3.68 from 10.08 to 13.74 milliequivalents of acid per gram of leonardite (MAF). This increase in total acidity was 89 per cent of the maximum expected increase. The maximum increase in acidity was observed for experiment 12 using the Marasse modification at 150°C and pressure of 1060 psig.

In the case of the Kolbe-Schmitt reaction in anhydrous form, the maximum increase in total acidity was 1.45 (from 10.08 to 11.53)

milliequivalents of acid per gram of leonardite (MAF) or 35.0 per cent of the maximum expected increase. The maximum increase in the carboxyl acidity was 26.6 per cent of the maximum expected increase. This increase was observed for experiment 2 using the Kolbe-Schmitt reaction in anhydrous form at 120°C and pressure of 920 psig for 8 hours.

The average per cent yield of humic acids was up from 77.7 per cent for raw leonardite to 90.4 per cent for carboxylated leonardite of experiment 12.

Generally the presence of moisture inhibits the introduction of a carboxyl group in the phenolic compound but the carboxylation has been successfully achieved in alkaline solutions for more reactive di- and trihydric phenols--especially where the hydroxyl groups are meta to one another. As elaborated earlier in the background section the humic acids of leonardite are of polyhydric type. Hence the carboxylation by the Kolbe-Schmitt reaction in slurry form may be possible. The reaction in slurry form is preferable because it eliminates the costly and time consuming operation of preparing and maintaining dry alkali salts of phenolic compounds. However, the results of experiments using the Kolbe-Schmitt reaction in slurry form did not show an increase in the acidities, and in fact showed a decrease. The reason may be that the hydroxyl groups in humic acids of leonardite are not meta to one another.

The results thus indicate that the Marasse modification is an improvement over the other two methods tried, viz., the Kolbe-Schmitt reaction in anhydrous form and in slurry form. The optimum conditions were found to be 150°C and pressure of 1060 psig for 8 hours.

The Kolbe-Schmitt reaction for carboxylation of alkali salts of phenolic compounds generally requires high pressures and high temperatures. An experiment was performed initially at 100°C and 295 psig for 4 hours to determine the minimum requirement of pressure and temperature. The results of analysis for this experiment showed that more drastic conditions were necessary. The temperature, pressure and time of reaction were all raised for subsequent experiments.

In the case of the Kolbe-Schmitt reaction, generally, an increase in pressure at a given temperature does not greatly affect the course of the reaction though in some cases the carboxylation rate may go up. Hence experiment 7 was carried out at an initial carbon dioxide pressure of 900 psig and a temperature of 150°C. The pressure during the reaction time of 8 hours was 1710 psig. There was a marked decrease in the acidities indicating decarboxylation of the reaction material. It was found that most of the reaction material, instead of being inside the liner, was lying in contact with the inside of the wall of the autoclave. The outside wall temperature of the autoclave was about 200°C. Thus the higher temperature may have resulted in decarboxylation and consequently in lower acidities. The scattering

of reaction material in the apparatus could have been as a result of the introduction of carbon dioxide. Another experiment was performed also at a higher starting pressure of 800 psig and was carried out for 24 hours (experiment 6). Carbon dioxide was introduced carefully so as to avoid scattering of the reaction material. The increase in the total acidity was only 7.0 per cent. This indicated that the time of reaction and pressure above a certain minimum value do not play a great role in this reaction.

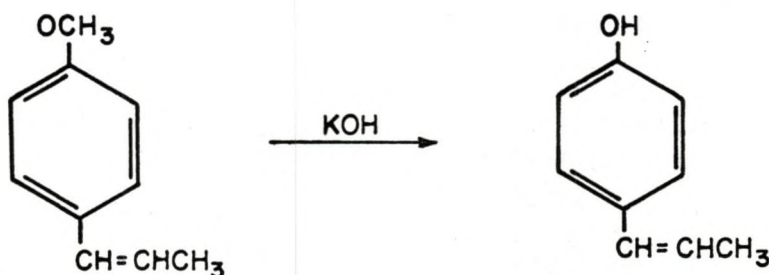
It was found that the lignite was not successfully carboxylated for the reaction conditions used in these experiments. Two experiments, 14 and 15, with lignite using the Kolbe-Schmitt reaction in anhydrous form were performed but the results showed no significant increase in total acidity.

It was observed that along with the increase in the carboxyl acidity, there was an unexpected increase in hydroxyl acidity also. The increase in hydroxyl acidity is advantageous in that the water solubility of leonardite is increased resulting in better emulsification. The total ion-exchange capacity is also increased which improves the performance of leonardite as a thinning agent.

Though the structure of humic acids of leonardite is not clearly defined, it is known that these acids have a stable structure whose properties are related to the presence of certain active functional groups. The functional groups found in the humic acids are phenolic

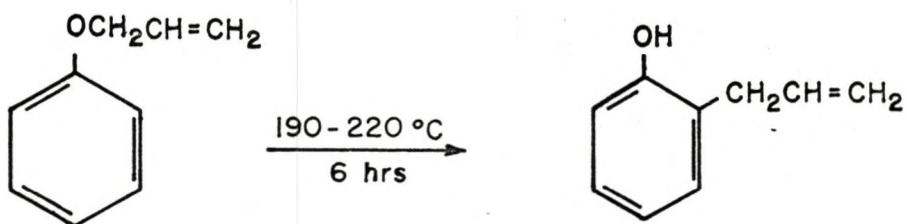
hydroxyl, carboxyl, carbonyl and methoxyl. The increase in the hydroxyl content of the leonardite could be explained with the help of the following reactions which may be possible for the functional groups present in humic acids of leonardite.

a) Anol is obtained by alkali fusion of the methyl ether, anethol, one of the chief constituents of oil of aniseed (8).

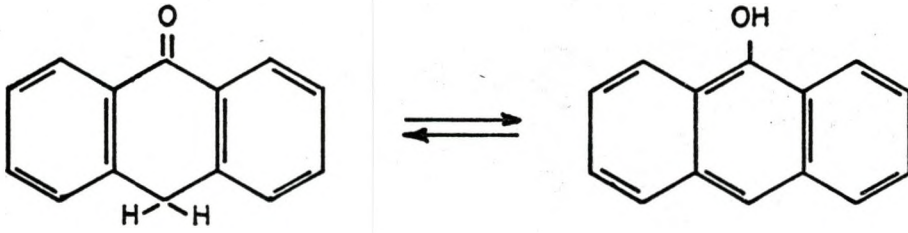


The excess potassium hydroxide present during carboxylation of leonardite at higher temperature may be converting the methoxyl groups of humic acids to hydroxyl groups.

b) Claison (9) discovered that phenol allyl ether when heated undergoes rearrangement to o-allylphenol.



c) Anthrone tautomerizes in warm alkali to the phenolic form (11).



The statistical interpretation of the data has been presented in Appendix C. The F test for the analysis of variance for the leonardite carboxylation indicates that changes in total and in carboxyl acidity are significant at the 0.01 level. The F test for the lignite experiments indicates that the change in acidity is not significant at the 0.05 level.

RECOMMENDATIONS FOR FURTHER WORK

This project did not involve attempts towards determination of structure of humic acids. Using the carbon dioxide tagged with carbon 14 for carboxylation it should be possible to determine the position of substitution of carboxyl group. The elucidation of structural changes taking place during carboxylation would also indicate the reason behind the increase in hydroxyl acidity. As indicated in the discussion of results the increase in hydroxyl content may be as a result of carbonyl group rearranging to form phenolic hydroxyl group or the methoxyl group converting to hydroxyl group in the presence of potassium hydroxide at high temperature.

Further work towards the effect of carboxylated leonardite on the properties of drilling fluid such as viscosity, gel strength and fluid loss should be done. Work in the direction of economic evaluation of carboxylated leonardite as a thinning agent for drilling fluids and binder for taconite pellets would be desirable. The increase in carboxyl acidity, hydroxyl acidity and the resulting increased ion-exchange capacity should make carboxylated leonardite a better thinning agent for drilling fluids and binder for taconite pellets.

SUMMARY

Leonardite was carboxylated at high temperatures and under carbon dioxide pressure using various carboxylation methods: the Kolbe-Schmitt reaction in anhydrous form, the Kolbe-Schmitt reaction in slurry form and the Marasse modification using anhydrous potassium carbonate. Temperature was varied from 100°C to 180°C and the initial carbon dioxide pressure from 225 psig to 900 psig. The time of reaction was also varied between 4 hours and 24 hours.

The results indicate that the Marasse modification gave the highest carboxylation and the highest increase in total acidity of leonardite among the methods investigated. The maximum increase obtained in carboxyl acidity was 39 per cent and that in total acidity was 89 per cent of the increase predicted on the basis of complete ortho substitution to all existing hydroxyl groups. The optimum conditions found were at 150°C temperature and a pressure of 1060 psig for 8 hours. It was observed that a longer time of reaction and higher pressure did not improve the results.

Increase in carboxyl and total acidity of leonardite using the Kolbe-Schmitt reaction in anhydrous form was 26.5 and 35.0 per cent respectively. The reaction conditions were 120°C temperature and

pressure of 920 psig for 8 hours.

Lignite did not show any significant increase in the total acidity for the reaction conditions studied in these experiments.

APPENDIX A

PREPARATION OF SAMPLE OF LEONARDITE

The leonardite used in this project was supplied by Baukol Noonan Company from Section 12, Township 162, Range 95, Burke County, North Dakota. A 30 pound sample was ground in a coal crusher and pulverizer to -325 to 170 mesh size.

After air drying the ground leonardite was subdivided by riffing to about two pound subsamples and stored in sealed cans. Each can was considered to be a representative sample.

APPENDIX B

SAMPLE CALCULATION

Run no. 2

Reaction conditions:

Temperature	120°C
Time	8 hours
Pressure	920 psig
Concentration of potassium hydroxide	0.369 N

Sample calculation:

Weight of leonardite	24.919 gms.
Less moisture (15.65%)	3.897 gms.
Less ash (11.45%)	2.853 gms.
Weight of MAF leonardite	18.167 gms.
Weight of KOH (375 mls. of 0.369 N)	7.766 gms.
Weight of reaction mixture	28.786 gms.

The weight ratio,

$$\frac{\text{MAF leonardite}}{\text{reaction mixture}} = \frac{18.167}{28.786} = 0.6311$$

Weight of sample for analysis	1.280 gms.
Weight of MAF leonardite in the analysis sample	
= 1.280 x 0.6311	0.806 gms.
Weight of humic acid obtained	0.632 gms.

Yield of humic acid as per cent per gram of

leonardite (MAF)	78.5%
Volume of solution for analysis of total acidity	44.0 mls.
Amount of hydrochloric acid (0.097) required to neutralize 10 mls. of aliquot for total acidity	5.7 mls.
Volume of solution for analysis of hydroxyl acidity	70.5 mls.
Amount of hydrochloric acid (0.097) required to neutralize hydroxyl groups of 25 mls. of aliquot	13.4 mls.
Normality of alcoholic caustic solution	0.235 N

Total acidity of sample is given by X

$$5.7 \times \frac{44}{10} \times 0.097 = (50 - X) \times 0.235$$

$$X = 39.5 \text{ mls.} \quad \text{----- (A)}$$

Hydroxyl acidity is given by

$$= 13.4 \times \frac{70.5}{25.0} \times \frac{0.097}{0.235} = 15.6 \text{ mls.} \quad \text{----- (B)}$$

Carboxyl acidity is given by (A) - (B)

$$= 39.5 - 15.6 = 23.9 \text{ mls.}$$

The acidities are tabulated as milliequivalents of acid per gram of leonardite (MAF). They are obtained after multiplying milliliters of acid by normality of alcoholic caustic solution and divided by the

weight of leonardite sample (MAF) for analysis.

Total acidity as milliequivalents of acid per gram of leonardite (MAF) is given by

$$= 39.5 \times \frac{0.235}{0.8061} = 11.52$$

Total Acidity per gram of leonardite (MAF)	Carboxyl Acidity per gram of leonardite (MAF)	Hydroxyl Acidity per gram of leonardite (MAF)
11.52	6.96	4.56

APPENDIX C

STATISTICAL INTERPRETATION OF RESULTS

The F-test for analysis of variance for total acidity and carboxyl acidity was used for the statistical interpretation of the data. The F values from tables correspond to 0.01 and 0.05 significance level for leonardite and lignite respectively. The F-test for leonardite was conducted for all the runs and the runs resulting in improved acidity.

TABLE 4

ANALYSIS OF VARIANCE FOR ACIDITY

Acidity in milliequivalents of acid per gram of raw material (MAF)

A) Total acidity of leonardite (all data)

Source of variation	Sum of squares	Degrees of freedom	Mean square	F computed	F 0.01
Between groups	96.26	14	0.88		
Within groups	0.72	16	0.04		
Total	96.98	30		152.89	3.46

B) Total acidity of leonardite (runs resulting in improved acidity)

Between groups	34.66	9	3.85		
Within groups	0.21	11	0.02		
Total	34.87	20		202.63	4.63

TABLE 4--Continued

C) Carboxyl acidity of leonardite (all data)

Source of variation	Sum of squares	Degrees of freedom	Mean square	F computed	F 0.01
Between groups	18.94	14	1.35		
Within groups	1.26	16	0.078		
Total	20.20	30		17.24	3.46

D) Carboxyl acidity of leonardite (runs resulting in improved acidity)

Between groups	8.17	9	0.91		
Within groups	0.18	12	0.015		
Total	8.35	21		60.53	4.39

E) Total acidity of lignite (all data)

Source of variation	Sum of squares	Degrees of freedom	Mean square	F computed	F 0.05
Between groups	0.24	2	0.12		
Within groups	1.64	5	0.33		
Total	1.88	7		0.37	5.79

APPENDIX D

TABLE 5

ANALYSIS AND SPECIFICATIONS OF LEONARDITE AND LIGNITE

SPECIFICATIONS:

	Leonardite	Lignite
Company	Baukol-Noonan Company	Baukol-Noonan Company
Seam	Section 12, Township 162, Range 95, Burke County, North Dakota	Section 4, Township 162, Range 94, Noonan Seam, North Dakota
Size	-325 to +170 mesh	-325 to +170 mesh

ANALYSIS:

	Leonardite (per cent)	Lignite (per cent)
Proximate (as received)		
Moisture	15.63	13.61
Volatile Matter	37.39	35.08
Fixed Carbon	35.66	43.65
Ash	11.32	7.66
Ultimate (MAF)		
Hydrogen	3.80	5.01
Carbon	65.26	72.42
Nitrogen	1.37	1.23
Oxygen (difference)	28.96	20.85
Sulphur	0.61	0.49

APPENDIX E

TABLE 6

DETAILED EXPERIMENTAL RESULTS OF LEONARDITE

Acidities in milliequivalents of acid per gram of leonardite (MAF)
and yield of humic acids as per cent per gram of leonardite (MAF)

Raw leonardite:

Total acidity	Carboxyl acidity	Hydroxyl acidity	Yield of humic acids (per cent)
10.02	5.88	4.14	78.9
10.08	5.97	4.12	78.9
10.25	6.00	4.25	74.1
9.97	5.91	4.06	78.9

TABLE 6--Continued

Carboxylated products:

A) The Kolbe-Schmitt reaction in anhydrous form

Expt. no.	Initial CO ₂ pressure	Temp.	Reaction pressure	Time	Total acidity	Carboxyl acidity	Hydroxyl acidity	Yield of humic acids
	psig	°C	psig	hrs.				per cent
1	225	100	295	4	10.00	5.73	4.27	78.5
					9.99	5.66	4.33	78.5
2	600	120	920	8	11.52	6.96	4.56	78.3
					11.53	7.12	4.41	77.5
3	600	150	1040	8	10.99	6.13	4.86	76.1
					11.12	6.52	4.73	79.2
4	620	150	1000	8	10.78	6.16	4.62	77.2
					10.83	6.02	4.80	79.5
5	600	180	1130	8	11.18	6.26	4.92	79.9
					11.52	6.48	5.05	80.0

TABLE 6--Continued

Expt. no.	Initial CO ₂ pressure	Temp.	Reaction pressure	Time	Total acidity	Carboxyl acidity	Hydroxyl acidity	Yield of humic acids
	psig	°C	psig	hrs.				per cent
6	800	150	1070	24	10.90	6.44	4.46	78.1
					10.65	6.11	4.55	80.9
7	900	150	1710	8	9.17	5.67	3.50	74.6
					8.85	5.29	3.56	73.6
B) The Kolbe-Schmitt reaction in slurry form								
8	600	150	960	8	8.31	5.09	3.23	73.7
					8.48	5.23	3.25	74.7
9	600	150	960	8	9.06	6.22	2.84	71.6
					8.62	5.83	2.79	69.2
10	600	180	1020	8	7.97	5.00	2.98	68.0
					7.12	4.44	2.68	67.4

TABLE 6--Continued

C) The Marasse modification using anhydrous potassium carbonate

Expt. no.	Initial CO ₂ pressure psig	Temp. °C	Reaction pressure psig	Time hrs.	Total acidity	Carboxyl acidity	Hydroxyl acidity	Yield of humic acids per cent
11	600	120	930	8	13.40	7.35	6.04	75.6
					13.53	7.49	6.05	75.8
12	600	150	1060	8	13.92	7.69	6.23	92.3
					13.56	7.45	6.11	88.6
13	600	180	1120	8	13.36	7.26	6.09	81.4
					13.39	7.39	6.00	77.4

TABLE 7

DETAILED EXPERIMENTAL RESULTS OF LIGNITE

Acidities in milliequivalents of acid per gram of lignite (MAF)
and yield of humic acids as per cent per gram of lignite (MAF)

Raw lignite:

Total acidity	Carboxyl acidity	Hydroxyl acidity	Yield of humic acids
(per cent)			
6.52	2.71	3.81	12.9
6.98	2.77	4.21	12.6

Carboxylated products:

The Kolbe-Schmitt reaction in anhydrous form

Expt. no.	Initial CO ₂ pressure	Temp.	Reaction pressure	Time	Total acidity	Carboxyl acidity	Hydroxyl acidity	Yield of humic acids
	psig	°C	psig	hrs.				per cent
14	615	150	1000	8	6.98	2.71	3.81	10.6
					6.67	2.77	4.21	10.6

TABLE 7--Continued

Expt. no.	Initial CO ₂ pressure	Temp.	Reaction pressure	Time	Total acidity	Carboxyl acidity	Hydroxyl acidity	Yield of humic acids
	psig	°C	psig	hrs.				per cent
15	700	150	1240	8	6.89	3.18	3.71	28.8
					6.84	3.06	3.78	28.5

BIBLIOGRAPHY

1. Abbott, G. A. "Our Growing Knowledge of Humic Acids," Proceedings of the North Dakota Academy of Science, XIII (July, 1959), 27.
2. Ibid., p. 30.
3. Ibid., p. 32.
4. Clem, A. G. "Role of Leonardite in Well Drilling Fluids," in Technology and Use of Lignite, compiled by Wayne R. Kube and James L. Elder, Bureau of Mines Information Circular, 8234, 99 (1964).
5. Ibid., p. 100.
6. Ibid., p. 101.
7. Ibid., p. 103.
8. Fieser, Louis F., and Fieser, Mary. Organic Chemistry (3rd. ed.; New York: Reinhold Publishing Corporation, 1956), p. 632.
9. Ibid., p. 639.
10. Ibid., p. 661.
11. Ibid., p. 768.
12. Fine, M. M., and Wahl, W. C. "Iron Ore Pellet Binders from Lignite Deposits," Bureau of Mines Report of Investigation, 6564, 1 (1967).
13. Fowkes, W. W., and Frost, C. M. "Leonardite: A Lignite By-Product," Bureau of Mines Report of Investigation, 5611, 5 (1960).
14. Ibid., p. 10.

15. Frost, C. M., Hoeppe, J. J., and Fowkes, W. W. "Source and Some General Properties of Humic Acids from Lignitic Materials," I. Chem. Eng. Data 4, 173 (1959).
16. Lindsey, Alan J., and Jeskey, Harold. "The Kolbe-Schmitt Reaction," Chemical Reviews, 57, 583-620 (1957).
17. Ibid., p. 583.
18. Ibid., p. 585.
19. Ibid., p. 587.
20. Ibid., p. 588.
21. Odenbaugh, M. L., and Ellman, R. C. "Leonardite and Other Materials as Drilling-Fluid Dispersants and Viscosity Control Agents," Bureau of Mines Report of Investigation, 7043, 1 (1967).
22. Ibid., p. 2.
23. Ibid., p. 6.
24. Purandare, Vijay R. "The Controlled Oxidation of Leonardite," Unpublished Master's thesis, University of North Dakota, Grand Forks, North Dakota, 1966.
25. Rogers, Walter F. Composition and Properties of Oil Well Drilling Fluids (3rd ed.; Houston: Gulf Publishing Company, 1963), p. 342.
26. Ibid., p. 370.
27. Ubaldini, I. "Some Information About Humic Acids," Brennstoff Chemie, 18, 273-292 (1937).
28. Youngs, R. W., and Frost, C. M. "Humic Acids from Leonardite: A Soil Conditioner and Organic Fertilizer," Proceedings of North Dakota Academy of Science, XVII (December, 1963), 77.
29. Ibid., p. 78.