

THE INTERACTION BETWEEN LIGNITE AND METHANOL

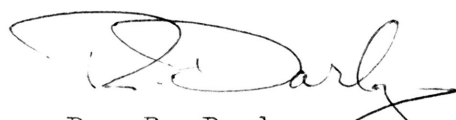
by

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## ABSTRACT

When Methanol is mixed with dried lignite, a vigorous reaction is observed. The reaction is exothermic, and the gas evolved is apparently carbon dioxide.

The purpose of this project is to determine the specific amount of carbon dioxide liberated. Two methods were tried: a volumetric method based on the absorption of carbon dioxide using a potassium hydroxide solution and a gravimetric method based on the adsorption of carbon dioxide using Ascarite particles. Texas Lignite from the Big Brown Mine in Fairfield Texas was used in the experiments and the samples were dried bone dry. The lignite particle size was -60+150 mesh for the first method and the -16+60 mesh was used in the second method. Consistent results were not obtained by either method. The most significant problem encountered was that carbon dioxide has a significant solubility in Methanol at low temperature. Thus, when Methanol was trapped or condensed out of the gas in the cold trap so that it could not get into the adsorption bottles, some carbon dioxide was lost. A better means of trapping or condensing Methanol without losing carbon dioxide has not yet been found.

Another alternative for determining the amount of

carbon dioxide was also suggested. The gas evolved from the Lignite-Methanol interaction would be allowed to bubble thru a 0.1N solution of a base, e.g. potassium hydroxide or sodium hydroxide. The resulting solution could then be titrated with a 0.1N solution of an acid, e.g. hydrochloric acid. The pH of the solution could be recorded as the volume of acid consumed increased. A titration curve could be drawn with the pH of the solution on the ordinate axis and the volume of acid consumed on the abscissa. The volume of carbon dioxide in the solution could then be determined. The dependability of the method has not been proved because of the limitation of the time allowed for the project.

Speculations as to the origin of the carbon dioxide suggested that carbonates in the lignite might decompose and contribute to the gas evolution. When hydrochloric acid was allowed to react with lignite, a gas liberation occurs. This fact is consistent with the idea that the source of the carbon dioxide might be from carbonates. However, when sodium carbonate or sodium bicarbonate was allowed to react with Methanol, no reaction could be detected. No definite conclusion could be drawn until further detailed studies are done.

## ACKNOWLEDGEMENT

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Dedicated to my parents  
and  
my fiancé

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## INTRODUCTION

Slurry pipelines are suggested as a means of transporting coal. Two water-coal slurry pipelines have been constructed, although currently, only one pipeline, the Black Mesa line, is operating. As the use of water-coal slurry presents some problems, such as the lack of water in the West (1), the great difficulty in the dewatering process of the coal, the problems involved in keeping the slurry suspended in pipes, etc ,... another medium, Methanol, has been proposed to replace water (2). Methacoal is a specific name for a Methanol-coal suspension made in accordance with a patented process (3). When Methanol and dried coal are mixed, a vigorous reaction occurs. The gas liberated has been identified by the chromatographic analysis to be predominantly composed of carbon dioxide.

The scope of this research project was to determine the amount of carbon dioxide gas generated per unit of lignite.

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The format and style of this thesis followed that of the Chemical Engineering Science journal.



## BACKGROUND

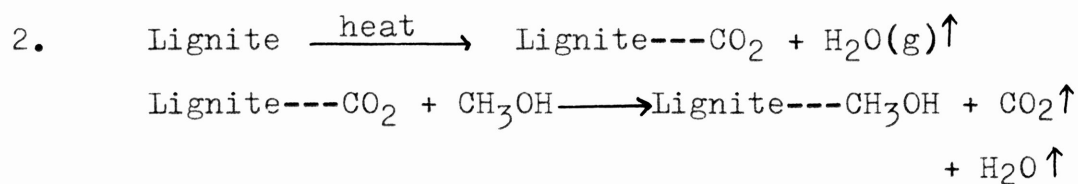
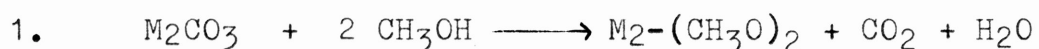
Methanol-coal suspensions, Methacoal, are thought to have advantages over water-coal slurries for several reasons. First, one must have considerable amount of fine particles for a water-coal slurry in order for it to be stable. Too many fine coal particles cause a problem in the dewatering process. Also, it is difficult to separate water from the fines, thus, the cost of dewatering is very high. In the other hand, owing to the high affinity of methanol for wetting the coal, i.e. methanol is uniquely absorbed by coal, Methacoal is a stable suspension. The separation of methanol from coal is quite easy owing to the volatility of methanol. Secondly, the water-coal slurry must be kept under high velocity in order to prevent settling. Therefore, the pumping cost and the maintenance cost are very high. Methacoal suspension can be transported with low turbulence. The flow can possibly be laminar. It is also more expensive to recycle the water than methanol due to the higher viscosity and density of water. Furthermore, Methacoal makes an excellent fuel for direct combustion in a boiler, or it could be used directly as a feed stock for chemical conversions to other products(4). In addition, as men-

tion previously, methanol and coal, when mixed, give off carbon dioxide gas. This gas evolution leaves the coal with more pores which increase the fragility, the porosity and the permeability of the particles. These particles are thus easier to grind and to pulverize, so that the power requirement for these processes also decreases.

Although some properties of methacoal slurries have been studied, much more information is needed before the use of methacoal pipelines are feasible. The viscosity of the slurry, which is a non-Newtonian fluid, has been measured as a function of shear rate, moisture content, particle size and concentration by Darby and Rogers (5), and the flow behavior was predicted. Studies are being done on the effect of methanol upon the hardness and the permeability of the lignite. The interaction between methanol and coal is an exothermic reaction and the heat of adsorption is also being studied.

The author has tried to determine the amount of gas liberated. However, the nature of the reaction has not yet been investigated. Speculations as to the origin of carbon dioxide evolution have indicated that compounds which contribute to the reaction are carbonates and carboxylic acids. Another mechanism was also suggested, which considered the possibility of some carbon dioxide molecules in the lignite itself. When the latter is dried,

the carbon dioxide-lignite bond becomes a weak bond. As methanol is added, it displaces the carbon dioxide molecules. Methanol molecules in turn become weakly bonded to the lignite structure. The possible reaction mechanisms for the reaction of carbonates with methanol and for the displacement of carbon dioxide were proposed as follows :



As previously indicated, these possible mechanisms were only gathered from speculations. No literature could be found on this aspect.

## EXPERIMENTAL

Instead of coal, the author used lignite for the experiments. Lignite, which came from the Big Brown Mine in Fairfield Texas, was donated by the Texas Utilities Company. Its initial moisture content was 25% by weight.

The lignite was ground using the jaw crusher and the ball mill. The ground lignite is then sized by a ro-tap and Tyler mesh sieves. Three sample categories were arbitrarily chosen. The coarse sample consisted of particles ranging from -16 Mesh to +60 Mesh (i.e. particle size smaller than 0.034 inches but larger than 0.0098 inches). The intermediate ranged from -60 Mesh to +150 Mesh (particles passing thru 0.0098 inches openings and retained on 0.0041 inches screen). The fine lignite consisted of -150 Mesh particles. Each sample category was then divided into smaller batches of lignite. The latters were dried to different moisture content levels (5 %, 15%, bone dry) in an oven at 105 degrees Centigrade.

Different methods for determining the amount of carbon dioxide evolved were tried. The first method was a volumetric method based on the absorption of carbon dioxide using a potassium hydroxide solution. The second

method was a gravimetric one based on the absorption of carbon dioxide using Ascarite solids. Each method will be discussed in detailed below.

After the crushing, grinding and drying steps, the experiment could be divided into two parts. In the first part, the carbon dioxide gas was generated using lignite and methanol. The amount of gas liberated was then determined in the second half of the experiment.

The gas generation step was the same for both methods mentioned above. One hundred grams (100g) of lignite was put in a closed flask. A vacuum was pulled in the flask for one minute to evacuate all the air. Methanol was then mixed with lignite at a methanol to lignite ratio of 2:1 . The evolution of gas bubbles was observed immediately. This reaction is exothermic. The whole system was allowed to reach equilibrium for thirty minutes.

In the first part of the project, the author used the first method to determine the volume of carbon dioxide generated. For a sketch of the apparatus, see fig 1. The mixing flask was connected to another flask containing acidified water. This flask is then connected to the Orsat analyser. The absorbant used in the Orsast was a solution of 40% by weight of potassium hydroxide. Carbon dioxide was bubbled thru the acidified water, then,

ORSAT

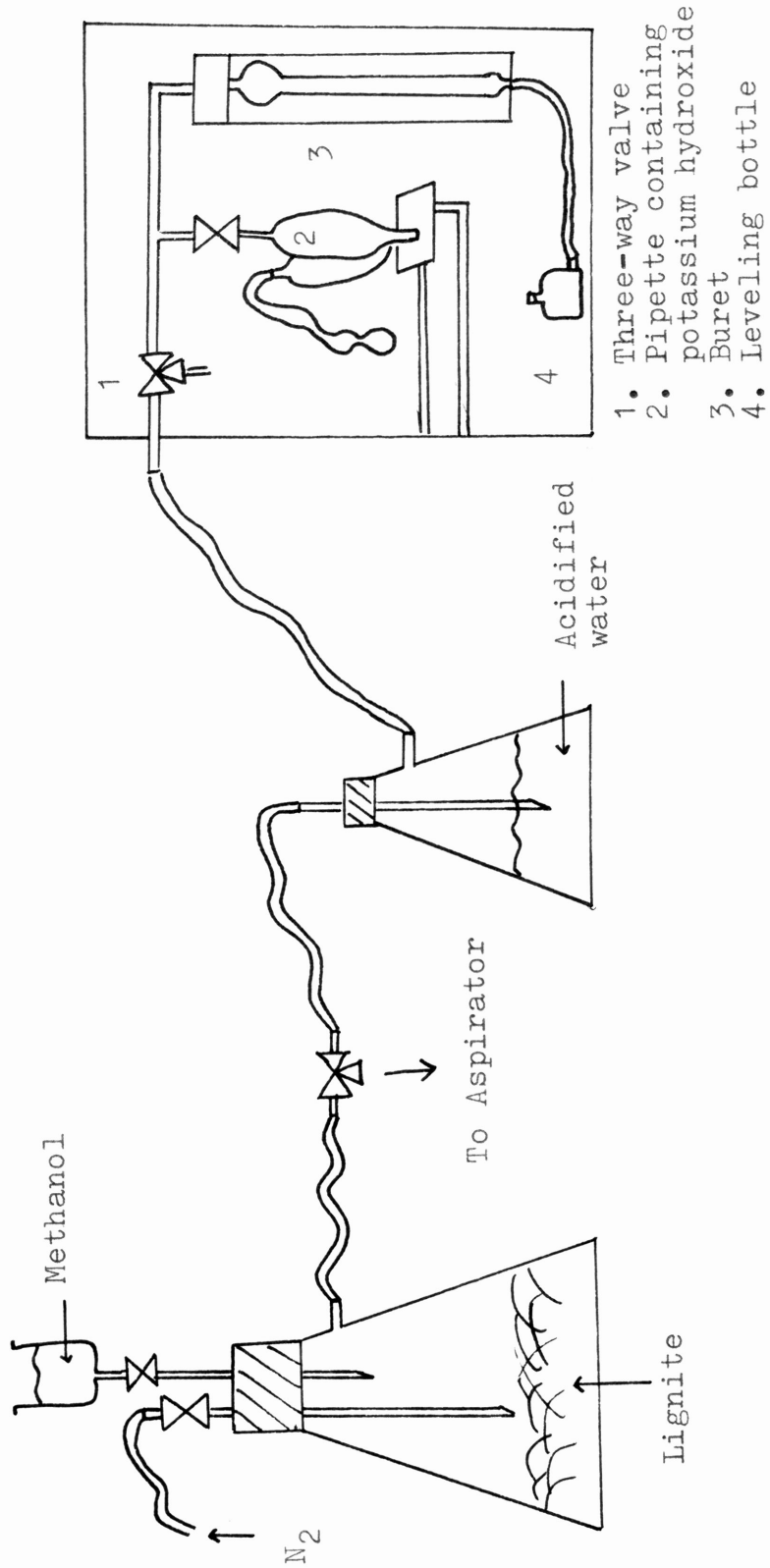
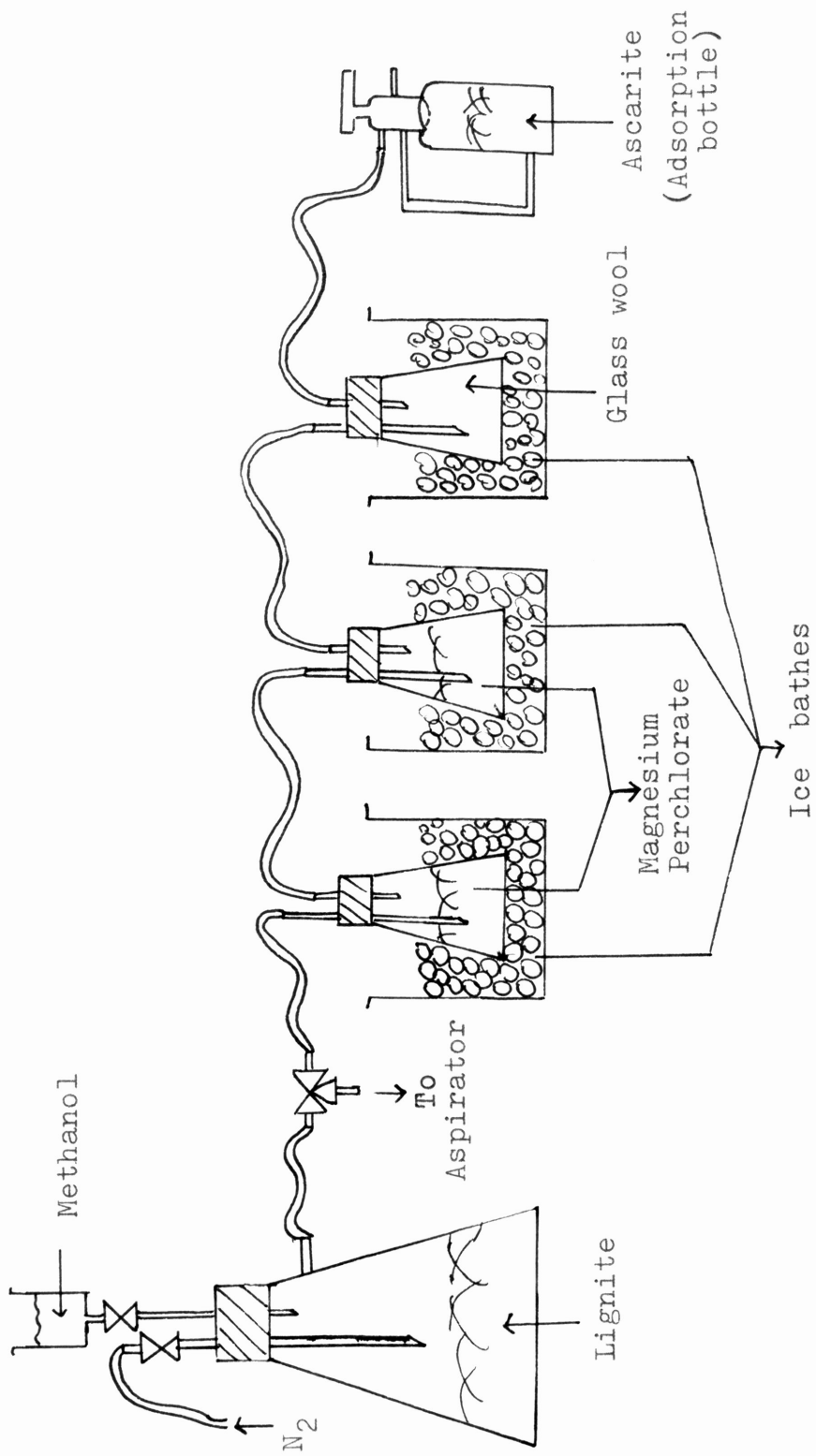


Figure 1: Apparatus for the determination of the amount of CO<sub>2</sub> by the first method: absorption of CO<sub>2</sub> by potassium hydroxide solution

it flowed into the Orsat where it is absorbed by the potassium hydroxide. The gas carrier used was nitrogen. As the interaction between methanol and lignite gives off heat, the methanol was partially vaporized. Thus, the purpose of the acidified water was to trap that vapor out of the gas stream. As the carbon dioxide was absorbed by potassium hydroxide, the volume of the initial input gas should decrease. The amount of carbon dioxide evolved could be determined by subtracting the initial volume of the gas to the final one. The author had used bone dry lignite of -60 Mesh to +150 Mesh as samples. For the operating procedure of the Orsat, see Appendix.

In the second method, a solid adsorption reagent, Ascarite, was used in place of potassium hydroxide solution. For a sketch of the apparatus, refer to fig 2 and fig 3. The methanol-coal reactor was connected to two flasks containing a drying reagent, Magnesium Perchlorate, and to a flask containing just glass wool. These flasks were emerged in ice bathes. Finally, an adsorption bottle containing Ascarite completed the system. The carbon dioxide gas was also swept out of the reactor, using nitrogen as a carrier, for one hour. The gas stream flowed thru the drying reagents where methanol vapor would condensed out. Any existing moisture was also trapped. The glass wool flask was mainly put in to



**Figure 2:** Apparatus for the adsorption of CO<sub>2</sub> using Ascarite particles (method 2)





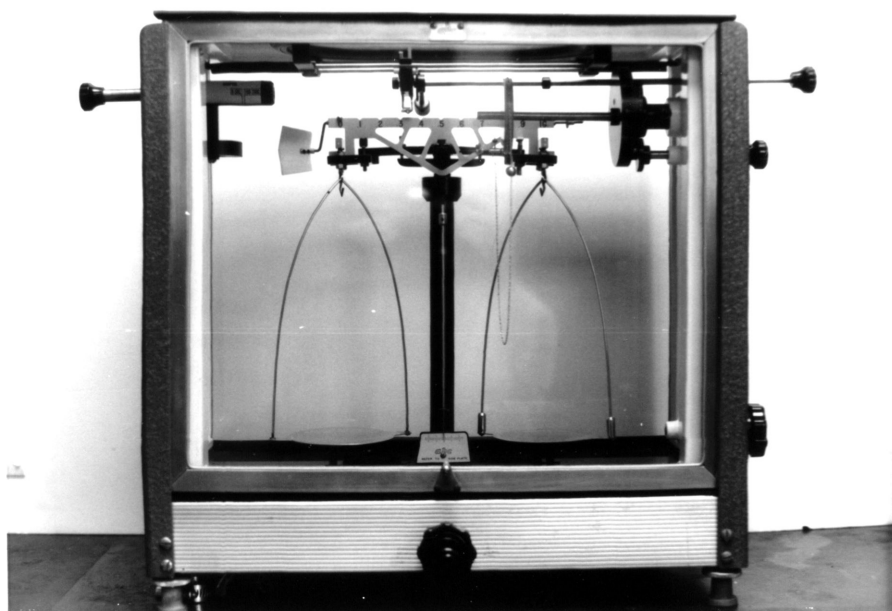
(a)

Figure 3 (a): Apparatus for method 2

capture any fine particles of Magnesium Perchlorate that might be carried by the gas stream. The Ascarite adsorbed the carbon dioxide gas. The amount of  $\text{CO}_2$  was determined by subtracting the initial weight of Ascarite used to the final weight. The analytical balance was used for all weight measurements. For the picture of the balance see fig 3 . Because it was very difficult and very time consuming to reduce lignite to a particle size less than 60 Mesh, using the existing equipments, the author had changed the lignite particle size from -60 +150 Mesh to -16+60 Mesh when this method was tried. Also, because of the lack of time, the author had not been able to analyse the gas evolved from partially dried lignite and methanol interaction. All samples were, thus, bone dry lignite.

For the flowchart of the experimental procedure, see fig 4.

Bone dry lignite of -16+60 Mesh was also reacted with hydrochloric acid in order to prove whether the source of  $\text{CO}_2$  were carbonates.



(b)

Figure 3 (b): Analytical balance used in method 2

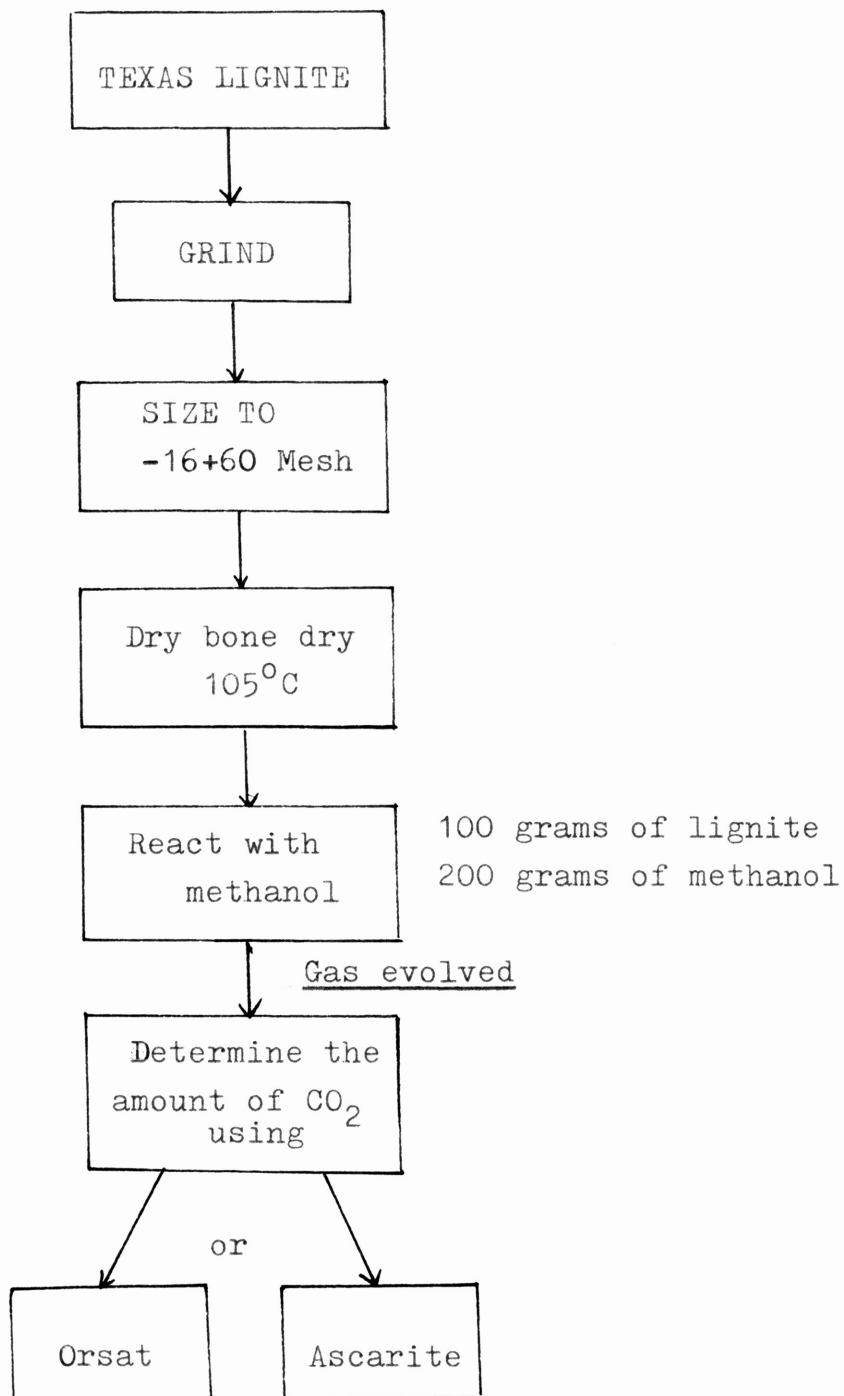


Figure 4: Flowchart of the experimental procedure

## RESULTS AND DISCUSSION

1)- Absorption of carbon dioxide by potassium hydroxide solution:

Using this method, the author was abled to obtain some result for only one trial. For 100 grams of -60 to +150 Mesh bone dry lignite, 8.6 milliliters of carbon dioxide was collected. Many more runs were done , but no results could be collected. No volume differences could be calculated. The initial volume of gas introduced into the Orsat repeatedly increased after the adsorption of carbon dioxide by potassium hydroxide solution. The probable reasons were that the gas might, initially, be under a pressure greater than atmospheric pressure. Then after the Orsat pressure equilibrated to atmospheric pressure, the gas expanded. The author had not yet been able to find out why the case occurred. Also, the author is, skeptical of the one result obtained. The reason being that no second result could be obtained in order to check the reproducibility of the data.

After doing ten experiments without any results whatsoever, the author, then, tried a second method which was the adsorption of carbon dioxide with Ascarite.

It was not until very recently, at the end of the semester, with the help of the advisor, the author had found out another probable cause of the failure of the first method. The error might be in the way of operating the Orsat. Unfortunately, because of the lack of time, the author had not been able to try this method again.

2)- Adsorption of carbon dioxide by Ascarite particles

Again, all the trials made with this method used 100 grams of -16+60 Mesh bone dry lignite . Two hundred grams or 252.7 milliliters of methanol were allowed to react with each sample. The results were listed in table 1.

As one can easily see the results were not very consistent. The inconsistency were due to numerous unforeseen problems. For trials numbers 1 and 2, only one flask containing the drying reagent, Anhydrous Magnesium Perchlorate, was in the system. This was not enough to capture all the methanol vapor and the moisture from the gas stream. The condensed vapor could be detected in the adsorption bottle containing Ascarite. Furthermore, the Anhydrous Magnesium Perchlorate particles had added some weight to the Ascarite. The very fine particles of the drying reagent were swept by the gas stream and deposited in the adsorption bottle. For trials 3

Table 1: Results for the adsorption of carbon dioxide  
by Ascarite method

<u>Trial</u>	<u>Weight of CO<sub>2</sub>(g)</u>
1	3.7961
2	4.0599
3	1.9547
4	1.0683
5	0.5070
6	0.4133
7	0.0045
8	0.0268
9	0.0233
10	0.0056
11	0.0002
12	0.0104
13	0.0037
14	0.0111
15	0.3103

and 4, another bottle of drying reagent and a bottle containing only glass wool were added to the system. Also, both drying reagent's bottles were equipped with glass wool. However, the methanol and the water vapors could still be detected on the Ascarite. For runs number 5 and thru 15, all bottles, except the adsorption one and the reactor, were emerged in ice bathes. It was not until then that condensation was no longer observed in the adsorption bottle. The results of the experiments were, however, still inconsistent. The possible reason for such scattered data was that, when methanol was condensed out, some carbon dioxide gas was also captured. The carbon dioxide gas, itself, will not condense either at room temperature, or a freezing temperature. The vapor pressure of carbon dioxide, at a temperature of 22.4 degrees Centigrades, is 60 atmospheres. At a temperature of -5.3 degrees Centigrade, its vapor pressure is 30 atmospheres (6). Thus, the only remaining reason might be that the carbon dioxide is soluble in methanol as it has been reported to be very soluble in alcohol. Therefore, the condensation method had proved to be not appropriate for the separation of methanol and carbon dioxide vapors.

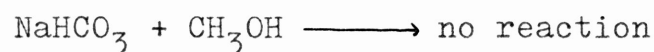
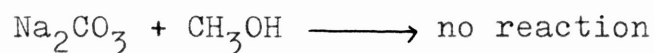
The amount of carbon dioxide trapped with methanol differed for each run. This phenomenon was probably due to the variation in the amount of methanol vaporized du-



ring each trial, as it was not possible to control the flow rate of the nitrogen, the gas carrier, flowing thru the system.

3)- Test for carbonates in lignite:

When lignite was mixed with diluted hydrochloric acid, bubbles of gas were given off. This fact proved that the carbon dioxide might come from carbonates of the lignite. However, a firm conclusion could not be drawn until the gas is analysed for  $\text{CO}_2$  and until the amount of carbon dioxide evolved from the lignite-hydrochloric acid reaction and that from the lignite-methanol can be measured and compared. It must be noted that, carbonates, under normal conditions, will not react with methanol. This fact was observed in the following experiments. Methanol was allowed to react with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and also with sodium bicarbonate ( $\text{NaHCO}_3$ ). The results were as followed:



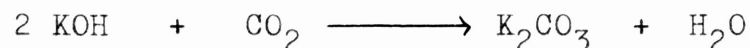
4)- Suggested method for the determination of  $\text{CO}_2$ :

Titration of  $\text{CO}_2$  in a basic solution with an acid.

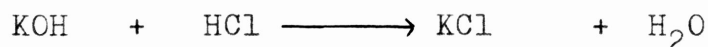
A titration method was suggested, but, again, because of the lack of the time, the author had not had the

opportunity to try. It was proposed that the liberated gas be allowed to bubble thru 0.1 N solution of a base (e.g. potassium hydroxide or sodium hydroxide solution) . After the carbon dioxide was absorbed by the base, the resulting solution could, then, be titrated with a 0.1N solution of hydrochloric acid. A pH meter could be used to measure the change in pH of the analysed solution as a function of the volume of the acid consumed. The plot of the pH versus the volume of HCl could be drawn. The resulting curve would be similar to the curve shown in figure 5. There would be three end-points.

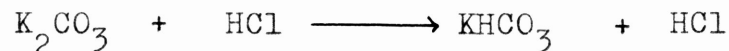
The initial reaction would be:



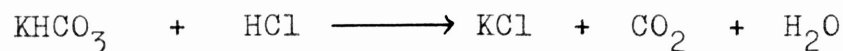
At end-point 1 , the reaction would be:



At end-point 2 , the reaction would be:



At end-point 3 , the reaction would be:



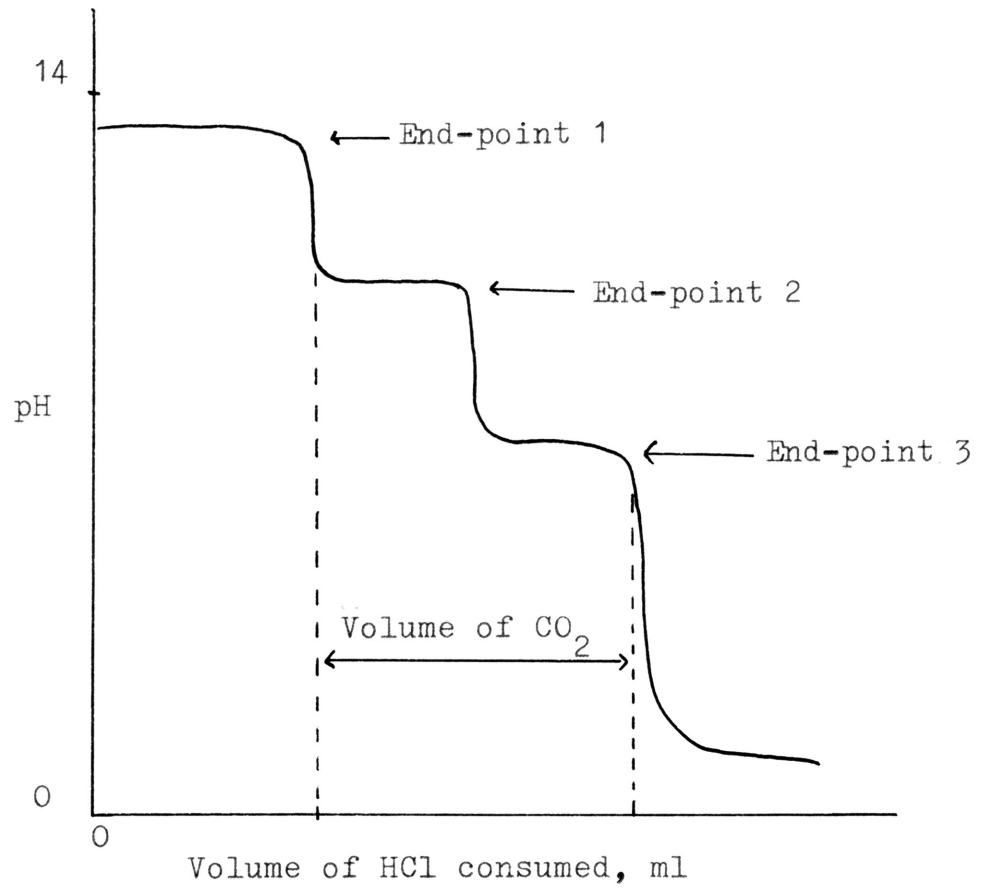


Figure 5 : Titration curve for Carbon Dioxide

## CONCLUSIONS

The determination of the specific amount of carbon dioxide by the absorption and the adsorption methods using respectively the potassium hydroxide solution and the Ascarite particles tried by the author had proved to be unsatisfactory unless a mean of separating carbon dioxide from the methanol vapor is found. Also, the amount of  $\text{CO}_2$  generated must be large. With methanol and lignite reaction, there was not enough gas to really get an accurate quantitative analysis with the cited methods. Some other more sophisticated methods should be used instead of the measurement of the volume difference or of the difference in weight ones. The titration method could be tried next.

As to the origin of the carbon dioxide evolution, no firm conclusion could be drawn yet. The gas could possibly from the carbonates of the lignite as the reaction of lignite with hydrochloric acid did give off gas bubbles. The  $\text{CO}_2$  liberated could also from the carbon dioxide in the lignite itself. The  $\text{CO}_2$ -lignite bond weakened as lignite was heated. When methanol was allowed to react with the heated lignite,  $\text{CO}_2$  molecules were displaced <sup>out</sup> ~~living~~ room for methanol molecules.

## APPENDIX

Operating procedure for the Orsat (7)(1) Preparation of potassium hydroxide:

40% solution (by weight).

Mix 160 grams KOH with 240 grams of distilled water.

The reaction is exothermic.

(2) The levelling bottle:

Fill with a solution of distilled water made slightly acidic by the addition of a few drops of an acid. Add a few drops of methyl orange. This makes the buret easier to read and also serves as an indicator of the accidental drawing over of a reagent during the run by turning from a pink color to a yellow one.

(3) Filling the pipette:

- Remove the rubber stoppers with attached expansion bags from the back side of the pipette.
- Add 180 to 200 milliliters of KOH to the pipette.
- Close all stopcocks. The three-way stopcock should be positioned so that the buret is closed to the at-

mosphere.

- Open the stopcock connecting the pipette with the buret. Lower the leveling bottle and draw the reagent up to the reference mark at the top of the pipette. Close the stopcock when the level reaches this mark. Do not draw the reagent into the stopcock or the manifold.
- If the level will not reach the mark, close the stopcock connecting the pipette with the manifold. Position the three-way stopcock so that the buret is open to the atmosphere. Raise the leveling bottle until the gas in the buret has been expelled.
- Reposition the three-way stopcock so that the buret is no longer open to the atmosphere.
- Repeat steps 4,5 and 6 until the level of the reagent can be adjusted to the reference line.

(4) Determination of the amount of CO<sub>2</sub> in the gas sample:

- Position the three-way stopcock so that the sampling bottle is connected to the buret.
- Lower the leveling bottle to draw a sample of the gas.
- When the level in the buret reaches the 0 milliliter mark, position the three-way stopcock so that the buret is closed to both the atmosphere and to

the sampling bottle.

- Raise the leveling bottle to place the gas in the buret under pressure.
- Open the stopcock to the pipette.
- Force the gas into the pipette by raising the leveling bottle until the confining liquid in the buret reaches the 100 milliliter mark. Do not force the liquid into the manifold.
- Draw the gas back into the buret by lowering the leveling bottle. Do not draw the reagent in the pipette into the stopcock or the manifold.
- Repeat steps 3 and 4 until there is no further decrease in the gas volume. (Usually this will be three or four passes.)
- Draw the reagent in the pipette up to the reference mark in the capillary of the pipette. Close the stopcock.
- Read the gas volume in the buret. The liquid level in the buret and that in the leveling bottle must be on the same horizontal plane. When reading the buret, the eye should be in the same plane as the water level.

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