การเตรียมถ่านกัมมันต์จากพีทโดยวิธีใช้ไอน้ำยิ่งยวดในฟลูอิไดซ์เบด

PREPARATION OF ACTIVATED CARBON FROM PEATS BY SUPERHEATED STEAM IN FLUIDIZED BED

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บทคัดย่อ

งานวิจัยนี้ได้ทดลองเตรียมถ่านกัมมันต์จากดินพีทของประเทศไทย โดยใช้กระบวนการเผาและกระตุ้นทางกายภาพ (ไอน้ำยิ่งยวดที่อุณหภูมิ 900°ซ) และเวลาตั้งแต่ 20-90 นาที ในฟลูอิไดซ์เบดผลิตภัณฑ์ที่ได้มีคุณสมบัติดังแสดง :-

ปริมาณถ่านที่ได้, %	8-55
พื้นที่ผิวอนุภาค, $ม^2/ก$	472-966
ค่าดูดซับสาร methylene blue, มก/ก	57.6-307.0
ค่าดูดซับสาร benzene, % (โดยน้ำหนัก)	27.5-92.9
ค่าดูดซับสาร iodine, มก/ก	571.3-998.4

จากผลการทดลองเบื้องต้นพบว่า อุณหภูมิที่เหมาะสมในการเผาเพื่อเตรียมถ่านพีท คือที่ 400-550°ซ และเวลาที่เหมาะสมในการกระตุ้นถ่านพีทที่อุณหภูมิ 900°ซ คือที่ 60-75 นาที ถ่านกัมมันต์ที่ได้มีคุณสมบัติเทียบได้กับผลิตภัณฑ์ทางการค้า และสรุปได้ว่าพีทดังกล่าวใช้เป็นวัตถุดิบในการผลิตถ่านกัมมันต์ได้โดยวิธีไอน้ำยิ่งยวดในฟลูอิไดซ์เบด

SUMMARY

Activated carbons were prepared from Thai peats by using carbonization and physical activation processes (superheated steam at 900°c) in fluidized bed for 20-90 minutes. The products obtained posses the following properties;-

Yield, %	8-55
Surface area, m^2/g	472-966
Methylene blue adsorption, mg/g	57.6-307.0
Benzene adsorption, % (by wt.)	27.8-92.9
Iodine adsorption, mg/g	571.3-998.4

The optimum conditions were found to be at 400-500°c for carbonization and at 900°c for 60-75 minutes for activation processes. The properties of the activated carbon obtained are quite comparable with the commercial ones. The Thai peat samples are therefore suitable to be used as raw materials for activated carbon production by superheated steam in fluidized bed.

INTRODUCTION

In commerical practice, most activated carbons are prepared by using carbonization and steam activation processes due to their low cost, easy operation and low pollution effect. Carbonaceous raw materials are to be carbonized before going through physical activation such as steam processing. During carbonization, materials are dried, degraded with the evolution of CO_2, CO, and acids, then decomposed to form tar, methanol and others. Carbonization is completed by heating at 400-600°C in closed system in order to attain the carbon product as high as possible. The carbon is then steam activated, the basic reaction of carbon with water vapour is :

$$C + H_2O = H_2 + CO \text{ (-31 kcal)} \quad (1)$$

The reaction and its kinetic has been studied extensively and discussed (1, 2)

Activation with steam is generally carried out at 750-900°C with the exclusion of oxygen which aggressively reacts with carbon and hence decreases the yield. It is noted that the oxides and carbonates of alkali metals, iron, copper and other metals catalyse the reaction of steam with carbon (2). An outline of the general technology on activated carbons from coal was presented (3). At the Government Industrial Development Laboratory, Hokkaido (GIDLH), studies on production of activated carbon from coal, wastes and wood materials by using fluidized bed carbonization and steam activation technique have been carried out (4,5,6). However, in order ot attain high quality adsorbents from various carbonaceous materials and effective processing techinques including high efficiency equipment, more researches and investigation on carbon activation are to be further carried out.

In this part of study, Thai peats which were found abundantly in the southern part of Thailand were used to be carbonized and steam activated. The carbon products were then analysed for their adsorption properties in order ot determine the possibility of using Thai peats as raw material for activated carbon production. Some preliminary study on using Thai peats to produce activated carbon was also studied at TISTR (6).

EXPERIMENTAL PROCEDURE

Raw material

Thai peat sample from the same source was from Prue Bajaw, Nara thiwat Province. The air-dried peats were used without crushing or pulverizing. Its proximate analyses and properties are shown in Table 1. Prior to

carbonization, the sample was ovendried at 105°C for more than 12 hours.

Procedures

Carbonization

Preparation of carbonized peats for steam activation at optimum temperature was proceeded in a metal box of $12 \times 12 \times 25$ cc size heated in a muffler furnace with moisture and volatile matter receiver (Fig 1). The carbonization time was kept for 3 hours at designated temperature for every experiments. About 700-900 g of peat was carbonized each batch. The carbonized peat was weighed, crushed with a steel roller (a diameter of 12cm), passed through standard sieves and determined for their size, proximate analysis and bulk density.

Steam activation

The carbonized peat of appropriate size was steam activated in a batch type fluidized bed reactor with external heat as shown in Fig 2. The reactor is made of stainless steel with inside diameter of 44 mm and total height of 535 mm (bed height of 305 mm). The conditions used in the experiments are as follows:

- about 100 cc (known weight) of char or carbonized peat per batch
- 1 ml/min of water flow rate for superheated steam generation
- 900°C activation temperature
- 20,30,40,50,60,75 and 90 min activation times

The reactor was heated to about 150-200°C with nitrogen flow continuously before the char was charged into the reator. The reactor was further heated up to the designed temperature or 900°C, then nitrogen was switched off while steam turned on to start the activation. The experiments were carried out at differents activation times as mentioned before. The activated carbon products were determined for their yields and adsorption properties.

Analyses

A. Proximate analyses

- Proximate analyses of the materials were carried out using the method based on JIS M 8812-1984 (Methods for Proximate Analysis of Coal and Coke) (8).

B. Thermal analyses

- DTA/TGA/TG curves of the materials and chemicals were determined using thermogravimetricdifferential thermal analyzer (TG-DTA) "RIGAKU" high temperature type and TG-DTA 2000 thermal analyzer system 001 of "Material Analysis and Characterization".

C. Surface areas

- Surface areas were measured by the single point BET method using QUANTASORB System, model no. QS-8.

D. Methylene blue adsorption

- Methylene blue adsorption were measured by using the method developed by the Government Industrial Development Laboratory, Hokkaido (GIDLH) (5).

F. Benzene adsorption

- Benzene adsorption value was measured by using the method developed by Hirata and co-workers (9) and modified by the GIDLH.

F. Iodine adsorption

- Iodine adsorption value was determined using the method based on JIS K 1474-1975 (Testing Method for Granular Activated Carbon) (10) with slight modification.

G. Pore size distribution analysis

- Pore size distribution analysis was determined by using "CARLO ERBA" Sorptomatic 1900 Series.

H. Bulk density

- Bulk density of the char was determined by using 10 ml measuring cylinder. A known weight of sample was put into the cylinder, tapped on the floor for 10 times before reading for its volume. The bulk density was then calculated.

I. Scanning electron microscope (SEM)

- The micrograph of the peat char was investigated by using JEOL JSM-T20 Scanning Microscope.

RESULTS AND DISCUSSION

Preliminary test of optimum carbonization temperature

From Fig 3, the DTA/TGA/TG chart shows that volatile matters in the peat evolve around 200 to almost 500°C temperature. The optimum carbonization temperature was considered to be about 400 to 550°C. The temperature used in this experiment was then considered to be 500°C.

Carbonization of peat

The average yield of the char carbonized in the metal box at 500°C is 52.6%. After crushing, the sieve analysis of the char particles was carried out and proximate analysis and bulk density of each size are determined as shown in Table 2 and 3 respectively. From the proximate analysis, the amount of ash increases inversely with the size of char while the fixed carbon increases with the size as expected. However, the volatile matter seems to fluctuate, which may be due to its high sensitivity to the analysis method used. For bulk density, the value decreases with size due to the high porosity of small size char. It is noted that the bulk density of the char particle size -0.5 + 0.297 mm is quite low. The reason my be due to the distinctly long shape of the char particle size -0.5 + 0.297 mm comparing to the others.

Steam activation of carbonized peat

Due to the size of the fluidized bed reactor, the char particles of size -1.41 + 0.297 mm were used to be steam activated. Size analysis of the particle char for steam activation is shown in Table 4.

The results on the effect of steam activation time at 900°C on yield, bulk density, ash content and adsorption characters of the activated carbon products are shown in Table 5. From the results it is noted that the yield and bulk density decrease with time. For ash content and adsorption characters of carbon products, they all increase with time. It is also seen that there are sharp increases after 50 min, however, leveling off after 75 min. When a semi-loga-rithmic plot of yield V.S. time was made (Fig 4), it is noted that there is a change in kinetic reaction rate at 50 min time. However, both reactions follow first order kinetics as follows:

$$\frac{w}{w_o} = Ae^{-kt}$$

where w_o = initial weight of char
w = remaining weight of char at reaction time(t)
k = apparent rate constant
A = constant

The apparent rate constants of the reactions were determined to be 15.90×3^{-3} and 36.60×10^{-3} min_{-1} respectively. The same result was also found when wood chars were steam activated (5), however, only one kinetic rate for each condition. There are 2 possible reasons for this incident of two kinetic rates, i.e.,

- there is a large amount of carry over product with the volatile matters especially after a long activation time (>50 min), larger char particle used may reduce the carry over.
- the char particles become smaller with higher ash content which then catalyze the reaction (2).

Further experiments to confirm these result should be carried on.

From the preliminary experiment, the adsorption characters of the activated carbon from Thai peats by steam activation are comparable to the commercial products after 60 min time (surface area 814-966 m^2/g, methylene blue adsorption 260.9-307 mg/g, benzene adsorption 71.2-92.9 wt% and iodine adsorption 922.4-998.4 mg/g). The adsorption properties are, consequently, lower than the products obtained from chemical activation due to high ash content (16.2-33.3% for 60-90 min activation time). The yield is also much lower (8.1-22.3%). In order to improve its adsorption properties, the carbon product (60 min activation time) was washed with 10% HCl solution (50 times weight by volume) for 24 hours. Its improving properties are shown in Table 5. The ash was removed about 40.7%, however, its adsorption characters do not increase as much a expected.

From the result, it is also show that the correlations between the surface areas and other adsorption properties tend to be linear.

CONCLUSION

Preliminary tests show that the optimum carbonization temperature for Thai peats was around 400-550°C. Thai peats were then carbonized in a metal box heated in a muffler furnace at 500°C for 3 hours and later steam activated batchwise in a fluidized bed reactor with external heat at 900°C for different period of times. The results show kinetic reaction rate changes at longer time, which may be due to large carry over or entrainment of the carbon products or the catalyzed reaction by the higher ash content after long activation time. Products of high adsorption characters (surface area 814-966 m^2/g, methylene blue adsorption 260.9-307.0 mg/g, benzene adsorption 71.2-92.9 wt% and iodine adsorption 922.4-988.4 mg/g) are obtained at activation time of more than 60 min with 8.1-22.3% yield, 0.12-0.19 g/cc bulk density and 16.2-3% ash content. Improvement on the adsorption properties was carried out by washing with 10% HCl, however, the properties do not increase much. The results also show that there are linear relationship between the surface area values and the other adsorption properties.

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TABLE 1. Typical proximate analyses and properties of Thai peats

Moisture, %	15.0
pH	3.6
Proximate analyses (dry basis)	
Volatile matter, %	61.4
Ash, %	3.1
Fixed carbon, %	35.5

TABLE 2. Size analysis of carbonized peat (char)

Particle Size (mm)	Weight (%)
+1.41	11.7
−1.41+1.0	36.1
−1.0+0.5	10.8
−0.5+0.297	18.6
−0.297	22.9

TABLE 3. Proximate analysis of Thai carbonized peats (different sizes)

	Size (mm)				
	+1.41	−1.41-1.0	−1.0+0.5	-0.5+0.297	−0.297
Moist, %	4.78	1.31	1.91	1.61	2.1
Ash, % D.B.	4.36	4.23	5.01	5.5	7.65
V.M., % D.B.	21.41	22.1	19.46	21.67	20.68
F.C., % D.B.	74.23	73.67	75.53	72.83	71.67
Bulk density, g/cc	0.46	0.43	0.38	0.33	0.4

TABLE 4. Size analysis of char particle for steam activation

Particle Size (mm)	Weight (%)
−1.41+1.0	56.6
−1.0+0.5	13.8
−0.5+0.297	29.6

TABLE 5. Effect of steam activation time at 900°C

Time (min)	Yield (%)	B.D. (g/cc)	Ash (%)	S.A. (m_2/g)	M.B. (mg/g)	B.A. (wt%)	I.A. (mg/g)
0	—	0.41	4.59	—	1.2	12.5	28
20	54.6	0.38	7.79	472	57.6	27.8	571.3
30	50.1	0.36	7.77	542	84.7	34.4	646.6
40	41.6	0.31	9.37	603	137.5	40.7	698.7
50	34.8	0.29	11.21	656	178.5	50.2	922.4
60	22.3	0.19	16.15	814	260.9	71.2	922.4
75	12.2	0.14	29.06	876	307	84.2	998.4
90	8.1	0.12	33.28	966	296.6	92.9	972.8
60 (washed)	95	-	9.58	839	274.8	71.8	875.3

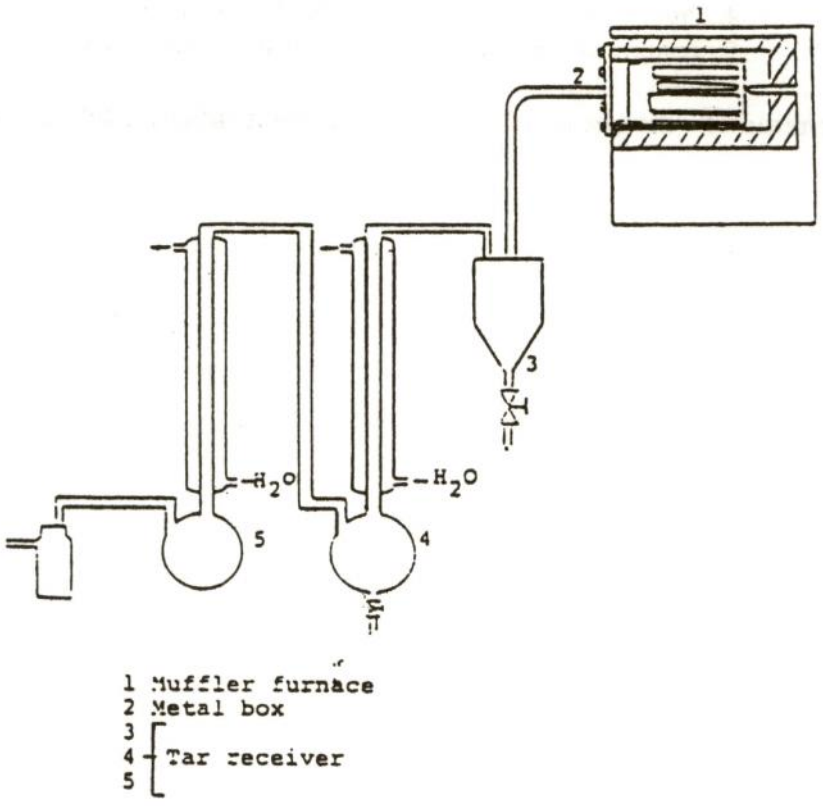
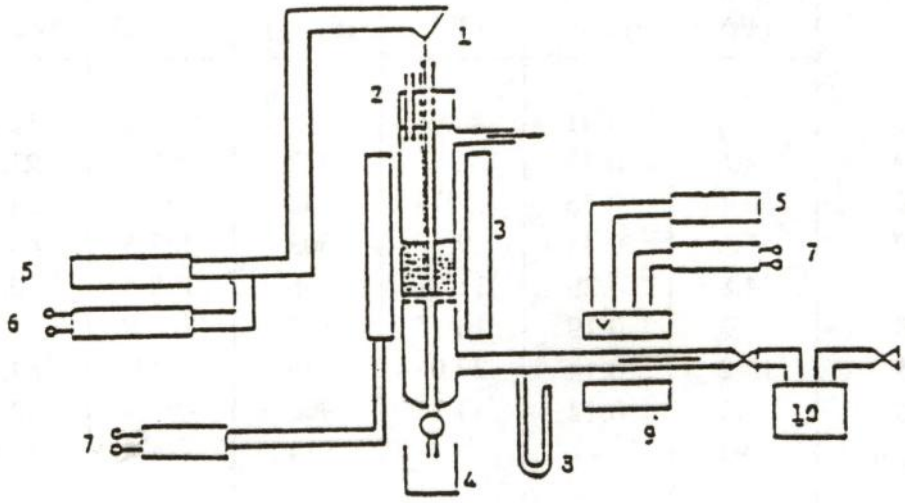


Fig. 1 Carbonization apparatus (muffler furnance)



1. Thermocouple
2. Sample inlet
3. Electric furance
4. Product receiver
5. Temperature indicator
6. Temperature controller
7. Electric transformer
8. Manometer
9. Heating band
10. Superheated steam boiler

Fig 2. Schematic diagram of activation apparatus (batchwise fluidized bed)

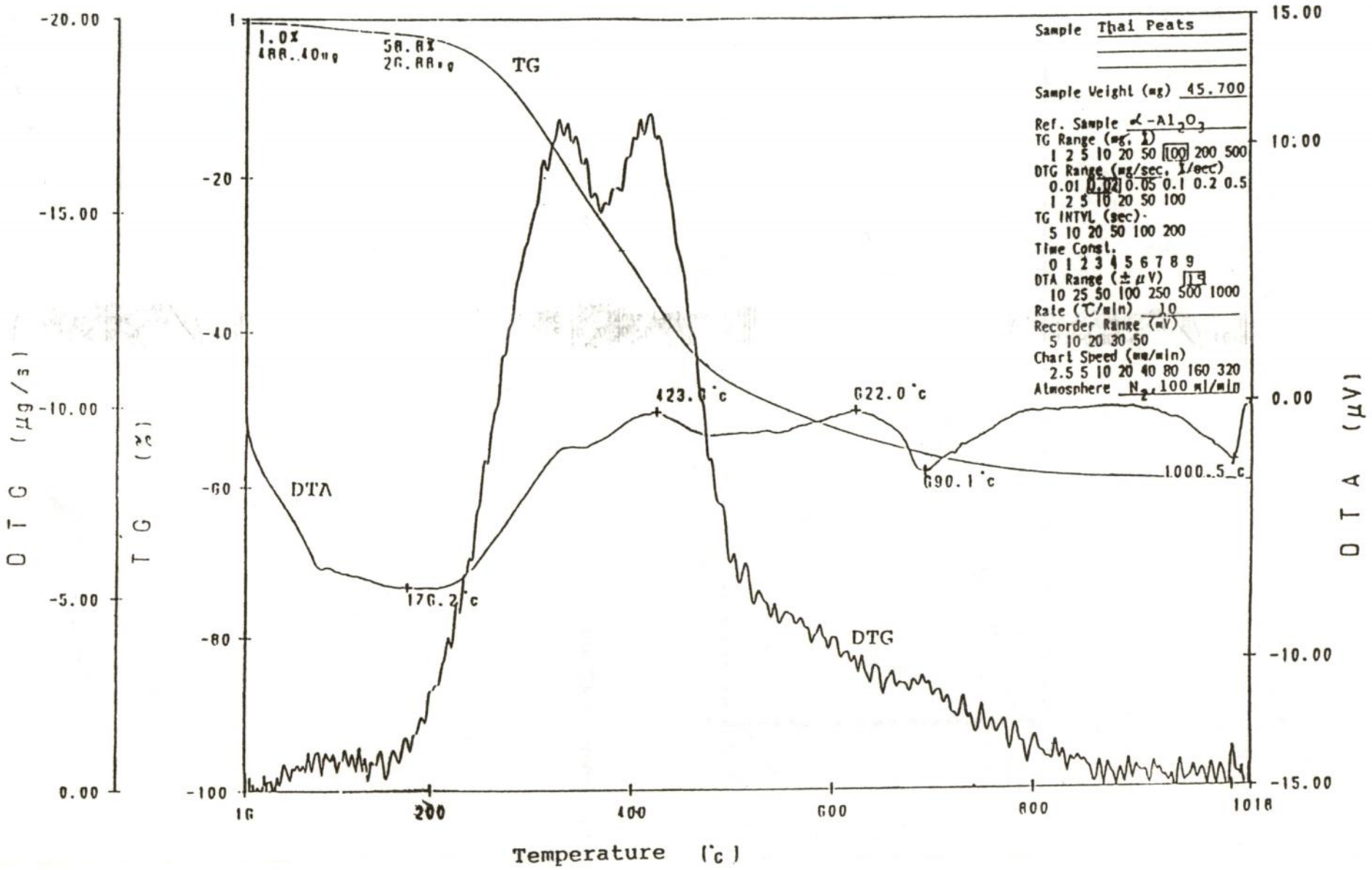


Fig 3. TGA/DTG/TG curves of Thai peat

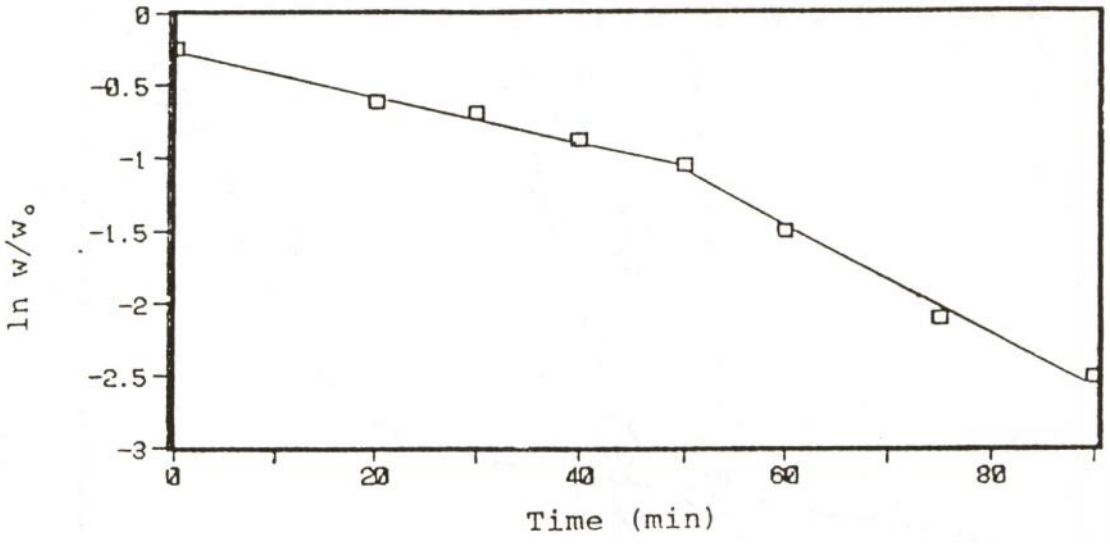


Fig 4. Semi-logarithmic plot of yield versus time for steam activation at 900°C