

EVOLUTION OF TARS AND GASES DURING
DEVOLATILIZATION OF COAL IN A FIXED BED REACTOR

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ABSTRACT

Devolatilization of a subbituminous coal has been investigated in a laboratory fixed bed gasifier, by contacting the coal with a reactive gas mixture similar to that entering the devolatilization zone of a commercial gasifier. Two particle sizes of feed coal PSOC-241 (-2,+1 and -4,+3 mm) at a single reactor pressure (30 psig) were evaluated, in the temperature range 350 to 550 C. The tars evolved were characterized by capillary gas chromatography and gel permeation chromatography. The tar and gas evolutions are described in terms of concentration and pressure profiles, through considerations involving diffusion and pore structure. The overall devolatilization rates are evaluated through the unreacted shrinking core model.

INTRODUCTION

In coal gasification, the objective is to increase the calorific value of the original raw fuel by removing the unwanted constituent, viz., ash, and also to produce a fuel which is cheaper to transport, handle and utilize. The present discussion will be limited to a Lurgi type fixed bed coal gasifier. Figure 1 [1] shows a schematic diagram of a Lurgi fixed bed gasifier. At the present state of technology, reliable engineering data are available on the gasification and combustion zones and can be readily applied to the design of a fixed bed gasifier. This is not the case with the devolatilization zone and no systematic study of the devolatilization phenomenon in the range of operating parameters for a fixed bed gasifier, has been reported in literature. Thus, it becomes necessary to conduct experimental and modelling work on the devolatilization behavior of coals, as influenced by particle size, pressure, temperature and a reactive gas environment [2]. Such devolatilization studies on a laboratory scale fixed bed gasifier form the main objective of the work described here [3]. The operating conditions for these studies are selected based on whatever data are available in the literature on fixed bed gasifiers, the approach being to simulate the conditions existing in the devolatilization zone of a fixed bed gasifier. The composition of the reactive gases entering the reactor is approximated to that entering the devolatilization zone of a fixed bed gasifier in practice. The residence time for the flow of reactive gases through the coal bed is

selected to be maintained at 5 seconds for all the runs. The results obtained from the devolatilization of a subbituminous coal, PSOC-241, at 30 psig (0.308 Mpa) reactor pressure are presented here. Two particle sizes of feed coal were evaluated: (-2,+1) mm and (-4,+3) mm. Reaction temperatures used were 350, 450 and 550 C. The H₂/CO mole ratio in the feed gas was maintained at 2.5. The duration of a devolatilization run was 5, 10, 20 or 30 minutes.

EXPERIMENTAL

A schematic representation of the experimental set-up is shown in Figure 2. The fixed bed reactor used for conducting the devolatilization studies was a 4.1 cm i.d. x 72 cm long 316 stainless steel tube provided with a wire mesh grid(0.25 mm opening), located 4 cm from the bottom, to hold the coal and char in the reactor. The reactor was placed vertically inside a furnace body. The graded coal sample was introduced into the reactor from the top under gravity by means of a Swagelok-type nut and feed pipe arrangement. Based on the reported gasification rates in a Lurgi type air blown gasifier [1,4] it was calculated that the entering gas environment in the devolatilization reactor should approximately have the following composition by volume:

Gas	H ₂	CO	CO ₂	CH ₄	N ₂	O ₂	Steam	Total
Volume%	18	7	14	4	25	2	30	100

Individual gases were drawn from compressed gas cylinders and mixed together with steam in a steam tube. The role of the steam tube was to convert feed water into steam, mix and preheat the steam-gas mixture to the desired devolatilization temperature. The steam tube was a 316 stainless steel tube(1.5 cm i.d. X 30 cm long), filled with inert catalyst support beads (3 mm diameter, alumina content=99% by wt. min; silica content =0.2% by wt. max; surface area=0.3 sq.m/gm; Norton Chemical Company) and was placed inside a small electric furnace. The feed gas stream entered the coal bed through a gas distributor located at the bottom of the reactor. A high pressure back pressure regulator after the condensers was used to maintain the desired pressure in the reactor system. The hot gases leaving the reactor from the top were laden with the tar generated inside the reactor; in order to quantitatively collect the tar and steam condensate, a double pipe heat exchanger was used as a condenser. Cooling water was circulated through the outer annulus and the tar laden gases were passed through the inner tube. Three such condensers (6mm i.d. X 40 cm long) were used in series to condense most of the tars. A high pressure glass fiber filter was used after the condensers as a final trap for the tar particles. After the completion of a run, methylene chloride was used as a solvent to wash down the condensers and the lines; dissolved tars and water phase were then collected from the bottom of the condensers. The yield of tar was measured in gm of tar per 100 gm of coal fed to the reactor. A Hewlett Packard 5840A gas chromatograph (with a 30 m long SE type 30 glass capillary column and a flame ionization detector (FID)) was used to quantitatively determine the species present in the tar samples. Area vs concentration curves for 30 standard species in methylene chloride were prepared. The species for standardization were selected

based on the published literature [5]. The molecular weights of tar samples were determined with a Waters Associates HPLC system. The columns used were 100 A and 500 A Ultrastaygel, made by Waters (columns: 7.8 mm i.d. X 30 cm long). The carrier solvent was tetrahydrofuran (THF) and a UV detector was used for absorption measurements. Polystyrene standards of known molecular weights were used to prepare a molecular weight vs elution volume curve.

The gas samples collected at 5, 10, 20 and 30 minutes from the sampling cylinders during the devolatilization run were analyzed for individual components. The permanent gases - CO₂, CO, and O₂ - were analyzed on a CARBOSIEVE S3 column and the hydrocarbon gases were analyzed on a PORAPAK R column. Both the columns were fitted on to a Hewlett Packard gas chromatograph 5840A equipped with an ECD detector. A MOLECULAR SIEVE 5A column was used on a Carle gas chromatograph 111H, equipped with a TCD detector to analyse the H₂ in the gas samples. N₂ was obtained by difference. At the end of a 5, 10, 20 and 30 minute run, the reactor was quenched in water and the char was removed and weighed.

RESULTS AND DISCUSSION

Chemical Analyses of Coal Sample

Table 1 gives the proximate and ultimate analyses of the subbituminous coal, PSOC-241. The coal sample was ground to minus 200 mesh U.S. sieve size and equilibrated to room conditions. The analyses were performed by the Continental Testing and Engineering Company, Vancouver, B.C., Canada. From these analyses, the value for the ultimate yield of volatiles was obtained as 50.07% of coal, to be used later in the kinetic models. In order to determine the effect of the duration of the devolatilization run on the total weight loss, some selected devolatilization runs were conducted for durations of 60 minutes and it was observed that there was no additional weight loss after 30 minutes from the start of the run. At 550 C, the maximum weight loss occurred equal to 49% of feed coal sample weighing 100 gm.

A. Devolatilization

Effect of Temperature

The principal effect of temperature on the devolatilization phenomenon is the decomposition of the organic structure of coal to yield water, hydrogen, methane, oxides of carbon and hydrocarbons. Consider the data on weight loss and tar/gas yields for the (-2,+1) mm and (-4,+3) mm size coal as shown in Tables 2 and 3. The weight loss is maximum at 550 C and is the least at 350 C. This confirms the earlier observation reported in literature about the nature of pyrolysis of

coal. At 350 C, the free moisture in the coal is removed and a small amount of tar is produced, which indicates that at this temperature, the majority of the coal chemical structure is still intact. At 550 C, most of the devolatilization is completed around 30 minutes as indicated by no additional weight loss during some runs conducted upto 60 minutes duration.

A plot of the distribution of molecular weights of tar samples is shown in Figure 3. From this it is clear that the fraction of evolving tar having molecular weight of about 300 units decreases as the run is continued. This can be attributed to the physical depolymerization of similar structures or the chemical cracking of a species to lower molecular weight as it is exposed to temperature for longer times.

The volumetric rate of evolution for all gases (Figures 4 and 5) shows a peak around 5 minutes from the start of a run and the rate then tapers off to zero around 30 minutes. In general, the rate of evolution for all gases is higher at higher temperature of reaction, i.e. $550 > 450 > 350$ C, for all particle sizes.

Effect of Particle Size

The runs at 30 psig reactor pressure in the reactive gas atmosphere did not exhibit any difference in the total weight loss for the two particle sizes of coal studied, at 550 C. For the (-2,+1) mm coal, the yield of tar at 30 minutes increased with temperature as shown in Table 3; whereas for the (-4,+3) mm coal, the yield of tar showed a maximum at 450 C, as shown in Table 2. This can be attributed to the cracking of tar at 550 C, resulting in reduced yield of tar at 550 C as compared to that at 450 C. Figure 6 shows the total weight loss and tar yield data for the two particle sizes. The tar molecules have longer residence time within the larger coal particles and hence the former are amenable to dissociation by cracking. The next section shows how the internal pressure build-up and tar concentration within the coal particle also increase with the particle size.

B. Mathematical Models for Devolatilization

Single First Order Reaction Model

The earliest approach to the mathematical description of the devolatilization phenomenon was that of Pitt (1962) [6] who proposed a simple first order rate expression for the overall rate of evolution of volatiles:

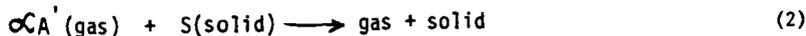
$$\frac{dV}{dt} = -kV \quad (1)$$

Anthony and Howard (1976) [7] have pointed out that this is an oversimplified description and the literature values for the activation

energy vary from as low as 4 kcal/mol to as high as 55 kcal/mol. This observation can be explained partly as being dependent on the type of the experimental set-up and operating variables, but mainly stems from the fact that when a series of parallel first order reactions are forced to be represented by a single reaction, very low values for the activation energy are bound to be obtained. In that respect, this representation is purely arbitrary but sometimes it has the ability of describing the observed rate process. Also, since there is often a limitation on analyzing the different chemical species quantitatively, such a simplified approach does have some merit. The values of activation energy and frequency factor for the subbituminous coal studied were: 11.4 kcal/mol and 0.554 1/sec for the (-2,+1) mm size coal; and 3.9 kcal/mol and 0.005 1/sec for the (-4,+3) mm size coal respectively. These indicate that although primary devolatilization involves organic reactions which have activation energy of the order of 50 kcal/mol, the first order approximation yields a very low overall value. Thus, it will be inappropriate to conclude from these low values that the devolatilization phenomenon is purely diffusion controlled. Of course there is a significant resistance to diffusion of volatiles through the ash layer, which will be evaluated later. A cross reference to the literature indicates that Shapatina et al., (1960) [8] have reported very low values for activation energy, viz., between 1 and 4 kcal/mol.

Unreacted Shrinking Core Model

This model was tested with the experimental data from the PSOC-241 subbituminous coal. The runs were conducted at 30 psig reactor pressure and in a reactive gas atmosphere. Two particle sizes of coal were used: (-4,+3) and (-2,+1) mm. The governing equation for this model is:



Fluid film resistance control

Equation (3) gives the necessary relation for fractional conversion of coal, for this case:

$$t/t^* = X, \quad t^* = R_p C_{SO} / 3k_{mA} C_A' O, \quad X = 1 - r_c^3 / R_p^3 \quad (3)$$

Based on equation (3), X, the fractional conversion of coal to volatiles was plotted against the reaction time. Figure 7 shows the data for (-2,+1) mm particle size, at 30 psig and reaction temperatures of 350, 450 and 550 C. The data points fall on straight lines, but since these lines do not pass through the origin, it is logical to assume that there is not significant resistance to diffusion in the gas film around the particles. Similar conclusions are arrived at for (-4,+3) mm size coal, as shown in Figure 8.

Ash layer diffusion control

Equation (4) gives the necessary relation in this case:

$$t/t^* = [1 - 3(1-X)^{2/3} + 2(1-X)] , t^* = \alpha R_p^2 C_{so} / 6 D_{eA} C_{A'O} \quad (4)$$

Based on equation (4), $[1 - 3(1-X)^{2/3} + 2(1-X)]$ was plotted against time, as shown in Figures 9 and 10. It appears that there is some resistance to diffusion within the ash layer and this will be examined further through equation (6).

Chemical reaction control

Equation (5) gives the necessary relation in this case:

$$t/t^* = [1 - (1-X)^{1/3}] , \sqrt[3]{t^*} = R_p / k_s C_{A'O} \quad (5)$$

Based on equation (5), $[1 - (1-X)]$ was plotted against time, as shown in Figures 11 and 12. These curves also indicate that there could be some reaction control on the progress of the coal devolatilization. This will also be further examined through equation (6).

Ash layer diffusion versus
chemical reaction control

Equation (6) gives the modified version of equation (4) as:

$$\sqrt[3]{t/t^*} = [1 - (1-X)^{1/3}]^2 , t^* = \alpha C_{so} R_p^2 / 2 C_{A'O} D_{eA} \quad (6)$$

$\ln[1 - (1-X)]$ was plotted against $\ln[t]$ as shown in Figures 13 and 14. Since the slopes of these lines are greater than two, it can be concluded that the ash layer offers the most of the resistance to the progress of coal devolatilization. This is further confirmed from Figure 15, where r_c/R_p is plotted against t/t^* as suggested by Levenspiel (1972) [10]. From this figure it is seen that the curve shows a point of inflection on the 135 degree dotted line (joining the points (0,1) and (1,0)), indicating that ash layer controls the progress of the reaction.

It must be pointed out at this stage that the above model is only 'phenomenological' and does not take into account the actual intrinsic chemical reactions. The numerous chemical species involved in devolatilization have been lumped into one hypothetical specie for the sake of mathematical simplicity and due to lack of detailed information on chemical structure. Thus this model is more qualitative in nature for this type of gas-solid system; it, however is quite informative.

Intraparticle Diffusion Model
for Subbituminous Coal [11]

This model has been described by Gavalas (1982) [11]. It describes the concentrations of tar and gas inside the coal particle as a function of radial position, temperature, pressure and experimental

yields of tar and gas. The principal equations describing this model are:

$$\frac{dC_G}{dr} = -\frac{\beta}{\mu} \frac{C_G}{D_{GK}} \frac{dp}{dr} - \frac{r}{3} \left[\gamma_G \left(\frac{x_T}{D_{GT}} + \frac{1}{D_{GK}} \right) - \gamma_T \frac{x_G}{D_{GT}} \right] \quad (7)$$

$$\frac{dC_T}{dr} = -\frac{\beta}{\mu} \frac{C_T}{D_{TK}} \frac{dp}{dr} - \frac{r}{3} \left[\gamma_T \left(\frac{x_G}{D_{GT}} + \frac{1}{D_{TK}} \right) - \gamma_G \frac{x_T}{D_{GT}} \right] \quad (8)$$

The analytical solution of these equations gives the dimensionless pressure build-up as:

$$W(0) - 1 = \frac{(-1 + A)}{A} \left\{ \left[1 + \frac{A_{at}(1 + \delta \xi_T) B}{(1 + A)^2} \right]^{1/2} - 1 \right\} \quad (9)$$

where

$$\xi = r/a, \quad V_i = C_i / (p_0 / RT), \quad (i = G, T), \quad W = p / \bar{p}_0$$

$$\delta = \gamma_T / \gamma_G, \quad \xi_T = D_{GK}^* / D_{TK}^*, \quad A = 3\beta p_0 / \epsilon \mu D_{GK}^*$$

$$B = RTa^2 \gamma_G / \epsilon p_{at} D_{GK}^*$$

The parameter 'A' in this model depends on bulk pressure outside the particles and on the temperature of the reaction. The parameter 'B' depends on the square of the particle radius. The differential equations describing the variation of tar and gas concentrations within the coal particle were solved on ACSL (Advanced Computer Simulation Language) and the following plots were made: The dimensionless pressure build-up, within the coal particle is plotted against the parameter A in Figure 16. This plot indicates that the pressure build-up is higher for larger particles. A plot of tar mole fraction within the particle against the radial position is shown in Figure 17. A plot for the tar concentration at the center of the coal particle with respect to parameter A (which is a measure of the total pressure on the system), is shown in Figure 18. This figure shows that for the pressure range investigated in the runs (30 - 375 psig) [3], the tar concentration is less sensitive to pressures upto 300 psig. Also, from these plots it can be seen that at a given pressure, the tar concentration increases with particle size.

CONCLUSIONS

The coal devolatilization experimentation reported herein involves realistic sizes of coal, and a reactive gas environment, as postulated to be present in the devolatilization zone of a Lurgi fixed bed gasifier, operating at a given pressure and temperature. No such work has been reported on a macrosample of coal and hence the results from the present work should be more meaningful. The conclusions to be drawn from the results presented are:

1. Devolatilization of coal is influenced by the operating variables.
2. The peak in molecular weight for the tar generated is around 300.
3. A first order approximation of the overall rate of devolatilization does not adequately describe the phenomenon.
4. The resistance to diffusion of tar out of the coal particle in the ash layer constitutes a major controlling mechanism in coal devolatilization.
5. Pressure build-up and tar concentration inside the coal particle both increase with particle size.

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NOTATION

a	radius of coal particle, cm
A	dimensionless parameter
A'	component in the gas phase
B	dimensionless parameter
$C_{A'0}$	bulk concentration of A' , gmol/cm ³
C_G	concentration of gas evolved, gmol/cm ³
C_{SO}	initial concentration of S , gmol/cm ³
C_T	concentration of tar evolved, gmol/cm ³
$D_{eA'}$	effective diffusivity of A' , cm ² /sec
D_{GT}	binary diffusivity, cm ² /sec
D_{iK}^*	Knudsen diffusivity of the i th component, cm ² /sec
D_{iK}	effective Knudsen diffusivity of the i th component, cm ² /sec
E	activation energy, kcal/mol
k, k_s	reaction rate constant, 1/sec
k_0	frequency factor, 1/sec
$k_{mA'}$	gas film mass transfer coefficient, cm/sec
p	pressure, atm
p_0	total bulk pressure, atm

P_{at}	atmospheric pressure, atm
r	radial position within the coal particle, cm
r_c	radius of unreacted core, cm
R	gas constant, cal/gmol. K
R_p	radius of coal particle, cm
S	component in the solid phase
t, t^*	time, sec
T	temperature, K
V	yield of volatiles, gm
w	fractional pressure build-up
x_T	mole fraction of tar evolved
x_G	mole fraction of gas evolved
X	fractional conversion
∞	stoichiometric coefficient
γ_T	rate of evolution of tar, gm/gm.sec
γ_G	rate of evolution of gas, gm/gm.sec
β	permeability of coal
μ	viscosity of gaseous mixture, cm^2/sec
E	voidage

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Table 1. Chemical Analyses of Coal Sample

Subbituminous Coal (PSOC-241)		Ultimate Analysis	
Proximate Analysis		% Carbon	66.17
% Moisture	10.81	% Hydrogen	4.53
% Ash	6.24	% Nitrogen	1.09
% Volatiles	39.26	% Chlorine	0.01
% Fixed Carbon	43.69	% Sulphur	0.39
	-----	% Ash	6.25
	100.00	% Oxygen	21.54
	-----		-----
Btu/lb	9941		100.00
free swelling index = 0			-----

Table 2. Volatiles, Tar and Gas Yields: PSOC-241 coal, (-4,+3) mm; reactor @ 30 psig; reactive gas + steam mixture

Total Volatile Yield, gm				
min	30	20	10	5
550 C	43.0	41.7	38.0	36.3
450 C	36.4	34.9	29.8	26.7
350 C	26.0	22.2	20.7	15.7
Tar Yield, gm				
min	30	20	10	5
550 C	1.75	1.07	0.77	0.31
450 C	2.17	0.89	0.80	0.74
350 C	0.75	0.53	0.45	0.28
Gas Yield, gm				
min	30			
550 C	13.7			
450 C	18.3			
350 C	6.3			

Table 3. Volatiles, Tar and Gas Yields: PSOC-241 coal, (-2,+1) mm; reactor @ 30 psig; reactive gas + steam mixture

Total Volatile Yield, gm				
min	30	20	10	5
550 C	42.9	42.2	37.1	35.8
450 C	37.0	36.8	33.5	31.9
350 C	24.0	23.8	23.4	21.5
Tar Yield, gm				
min	30	20	10	5
550 C	1.90	1.3	0.85	0.64
450 C	1.47	1.17	1.05	0.55
350 C	0.82	0.65	0.4	0.3
Gas Yield, gm				
min	30			
550 C	19.7			
450 C	7.3			
350 C	N.A.			

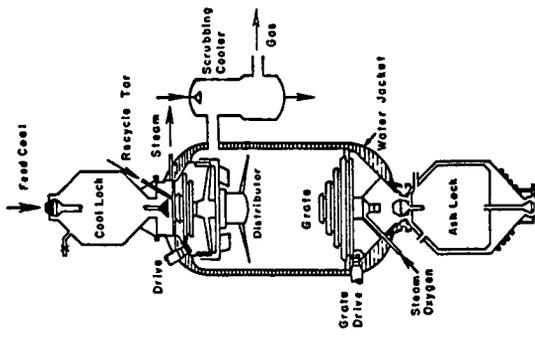


FIG. 1 - LURGI PRESSURIZED GASIFIER [1]

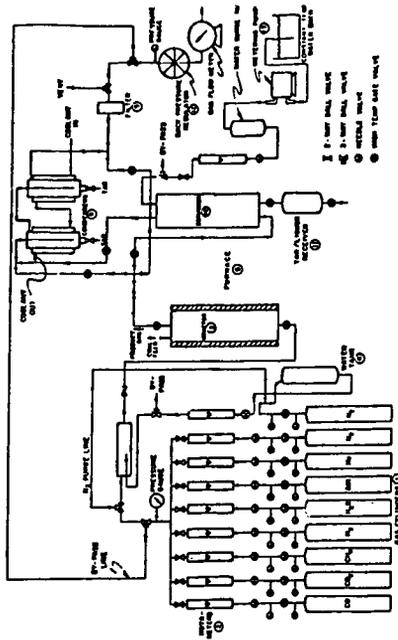


FIG. 2 - EXPERIMENTAL SET-UP [3]

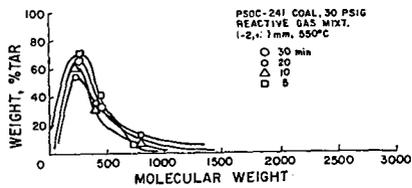


FIG. 3 - MOLECULAR WEIGHT DISTRIBUTION OF TAR

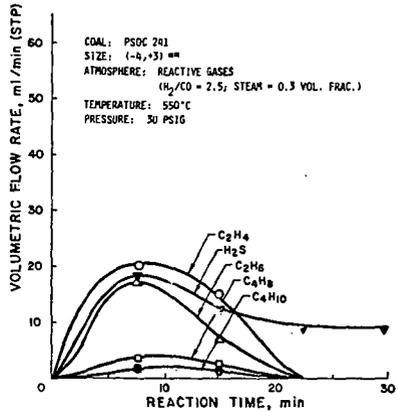


FIG. 5 - GAS EVOLUTION RATE VS. TIME
 (HYDROCARBON GASES EXCL. METHANE AND INCL. H₂S)

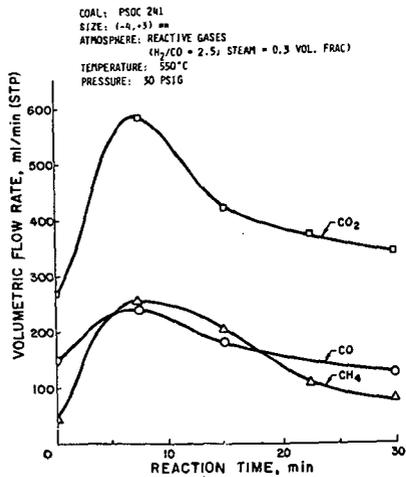


FIG. 4 - GAS EVOLUTION RATE VS. TIME
 (PERMANENT GASES INCL. METHANE)

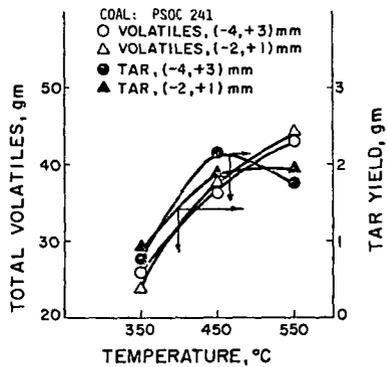


FIG. 6 - EXPERIMENTAL DATA

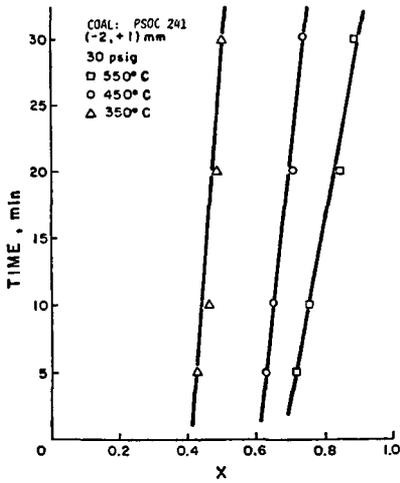


FIG. 7 - FLUID FILM RESISTANCE CONTROL, TYPE I

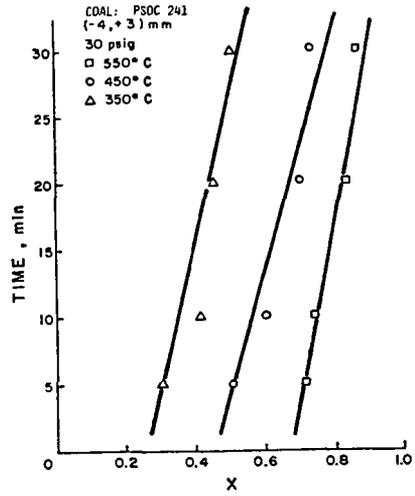


FIG. 8 - FLUID FILM RESISTANCE CONTROL, TYPE I

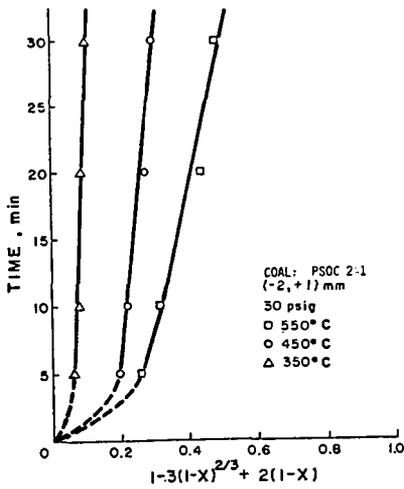


FIG. 9 - ASH LAYER RESISTANCE CONTROL, TYPE II

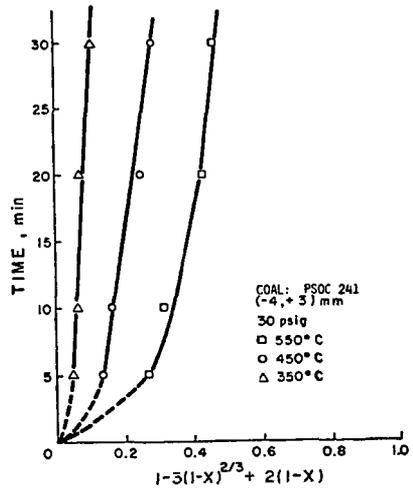


FIG. 10 - ASH LAYER RESISTANCE CONTROL, TYPE II

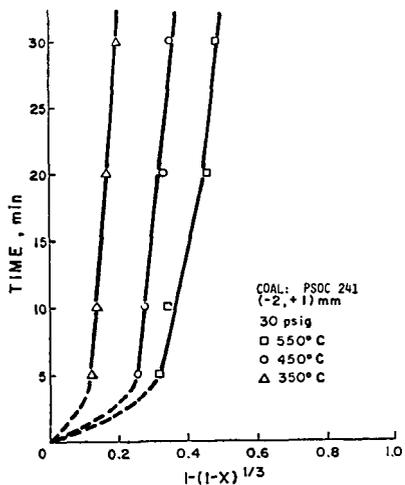


FIG. 11 - CHEMICAL REACTION CONTROL, TYPE III

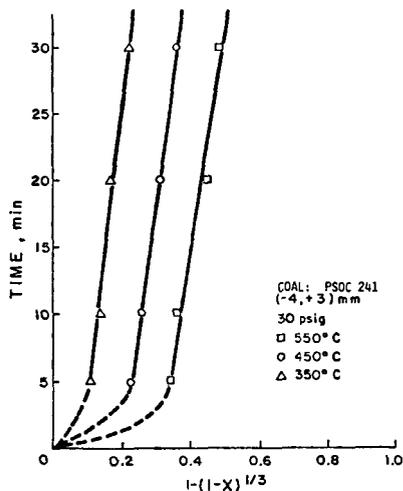


FIG. 12 - CHEMICAL REACTION CONTROL, TYPE III

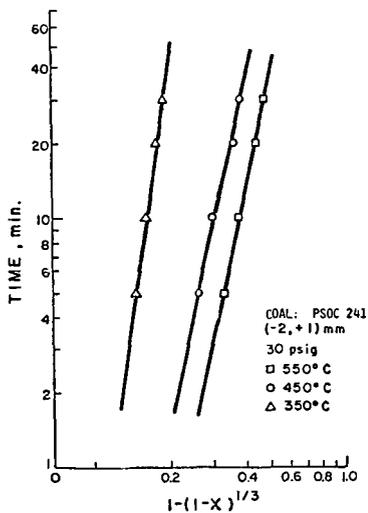


FIG. 13 - ASH LAYER RESISTANCE CONTROL, TYPE II'

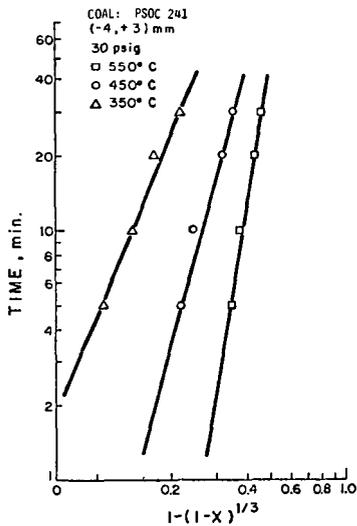


FIG. 14 - ASH LAYER RESISTANCE CONTROL, TYPE II'

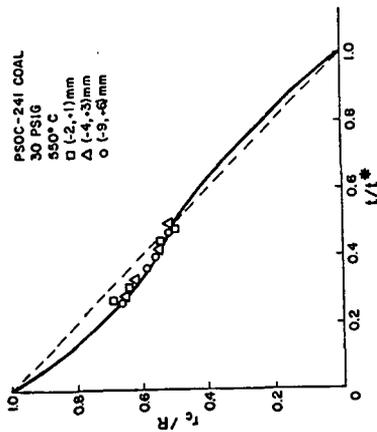


FIG. 15 - UNREACTED SHRINKING CORE MODEL

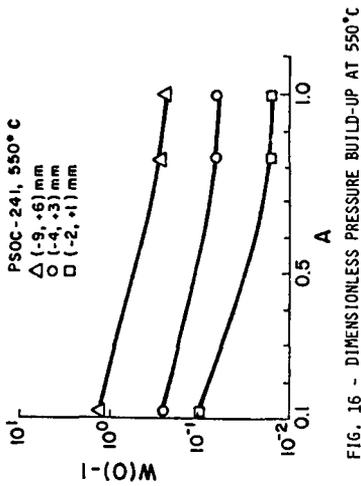


FIG. 16 - DIMENSIONLESS PRESSURE BUILD-UP AT 550°C

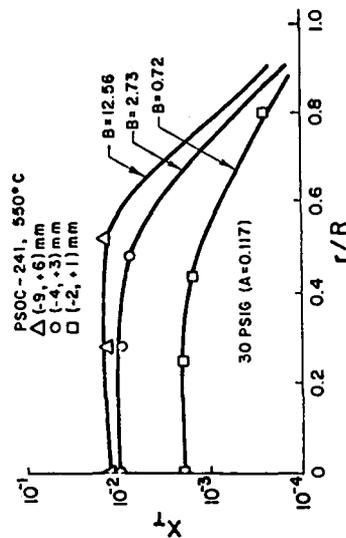


FIG. 17 - TAR MOLE FRACTION INSIDE COAL PARTICLE

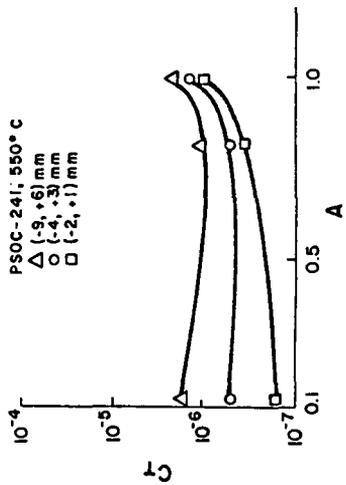


FIG. 18 - TAR CONCENTRATION AT THE CENTER OF COAL PARTICLE