

Kinetic Studies on Physical and Chemical Activation of Phenolic Resin Chars

Damyanti Agarwal, Darshan Lal, V. S. Tripathi* and G. N. Mathur

Defence Materials Stores Research and Development Establishment, G.T. Road, Kanpur – 208013

*e-mail: dmsrde@sancharnet.in

(Received August 21, 2003; Accepted September 25, 2003)

Abstract

Granular Activated Carbon (GAC) has been proven to be an excellent material for many industrial applications. A systematic study has been carried out of the kinetics of physical as well as chemical activation of phenolic resin chars. Physical activation was carried out using CO₂ and chemical activation using KOH as activating agent. There are number of factors which influence the rate of activation. The activation temperature and residence time at HTT varied in the range 550–1000°C and ½ ~ 8 hrs respectively. Kinetic studies show that the rate of chemical activation is 10 times faster than physical activation even at much lower temperature. Above study show that the chemical activation process is suitable to prepare granular activated carbon with very high surface area i.e. 2895 m²/g in short duration of time i.e. 1 to 2 hrs at lower temperature i.e. 750°C from phenolic resins.

Keywords : Activated Carbon, Resins, Char, External surface area, Activation energy, order of reaction

1. Introduction

The kinetics of carbon char gasification have been the subject of innumerable theoretical and experimental studies. Most commonly, the gas reactions of carbons are treated as conventional heterogeneous gas solid reactions in which the rate is proportional to the total accessible surface area of the solid. Typically, these are the reactions of carbon with oxygen or air, steam and carbon dioxide. The carbon involved in reaction may be one of many diverse forms ranging from its well - developed crystalline structures, graphite and diamond, to amorphous varieties such as carbon black, cokes and chars.

Impetus for studies of the kinetics of these carbon reactions is derived quite apparently from their manifold industrial applications. The carbon oxygen reaction is the basis of the direct generation of most of our electrical energy from coal. Indirectly, the carbon - steam reaction also serves as an important source of energy. Apart from the production of energy in the form of electricity or gaseous fuels, there are many practical applications in which the reaction of carbonaceous materials with aforesaid gases needs either to be promoted or suppressed such as manufacture of activated carbon. The use of graphite as a moderator material in nuclear reactors has created a new need for minimizing the reaction of carbon with its ambient atmosphere. In these various adaptations of carbon gasification reaction fundamental knowledge of the reaction

mechanism and kinetics is essential for the proper design and control of the process [1]. There are a number of factors, which influence rates of reactions. Some of these are concentration of reacting gas when a diluent is used for better control over reaction rate, temperature of the system, residence time, nature of the reactants and products, presence of catalyst, and last but not the least surface area of reacting solid (char). In the preparation of controlled porosity activated carbon, gas solid reaction involving chars of natural or synthetic polymers and steam or carbon dioxide is a key step. Chemical activation is also used for this purpose in which potassium hydroxide and phosphoric acid are used as activating agent. Keeping in view the above factors we studied the effect of heat treatment temperature, residence time and type of polymeric chars on the activated carbon yield and surface properties by both chemical and physical activation method to determine the kinetics of activation and to evaluate the complete rate equation. The catalytic effect of potassium on carbon gasification and rate of activation was also studied.

In the present work, a systematic study has been carried out to prepare activated carbon having a wide range of surface properties from two types of phenolic resins. These resins are designated as PFR1 and CFR1. Both of these resins were prepared in excess of formaldehyde in basic pH range using triethyleamine as catalyst. In PFR1 phenol and formaldehyde and in CFR1 m-cresol and formaldehyde were used as reactants.

2. Experimental

2.1. Materials

In the present investigation, the phenolic resins used for carbonization and activation were synthesized in the lab. The materials used in the process were phenol LR Grade of Ranbaxy Laboratories Ltd., formaldehyde (37%) solution in water provided by Sarabhai Chemicals, ammonia solution (30%) and hexamethylenetetramine (LR) of S.D. Fine Chemicals, and triethylamine (99%) of Lancaster and methanol AR grade of Qualigens Fine Chemicals.

2.2. Product Preparation and Experimental Setup (Fig. 1)

The resins used as precursor material for kinetic study were prepared in the laboratory. Resins were prepared using phenol and formaldehyde reactants in 1:1.5 molar ratio. The details of the resin preparation procedure is given elsewhere [2]. A series of activation experiments were carried out to study the effect of highest treatment temperature (HTT), hold up time and the activation method on the properties of end product and on the rate of reaction. Resin chars were prepared by heating these resins at a heating rate of 10°C/min upto 700°C in an inert atmosphere and kept at this temperature for half an hour. Further for physical activation, resins were heated in CO₂ atmosphere at a heating rate of 25°C/min upto HTT at the CO₂ flow of 50 ml/min in a vertical tubular furnace ID 22 mm. This flow rate was selected after a number of experiments because at this flow the effect of bulk diffusion was found minimum. The highest treatment temperature was varied from 750 to 1000°C and holds up time at HTT from 2 to 8 h.

In chemical activation method resin chars were mixed with KOH in 1:4 char to KOH ratio by weight approximately. Mixing was performed at 85°C. Afterward mixture was dried at 110°C. After drying the mixture in a silver boat the chemical activation was performed in a two zone horizontal tubular furnace housed a long quartz tube which could be pushed into heated zone when desired temperature is attained. The temperature was further raised to highest

activation temperature i.e. 550~750°C at the rate of 25°C/min. In the meantime the dried sample was kept in the zone maintained at 110°C. When the HTT is attained the sample pushed in and activated for 30 to 120 mins in N₂ atmosphere. After cooling the mixture in inert atmosphere, mixture was treated with 0.5 N HCl and washing was performed upto neutral pH.

3. Results and Discussion

3.1. Kinetics of Physical Activation

Several experiments were carried out for activation of two resin chars namely PFR1 and CFR1 using CO₂ as activating agent. The kinetics of reaction was followed by noting the weight change with time. Usually three resistances in solid gas reactions i.e. gas film, surface reaction and ash layer controls the progress of reaction. The relative roles of these three resistances can be given by [3]:

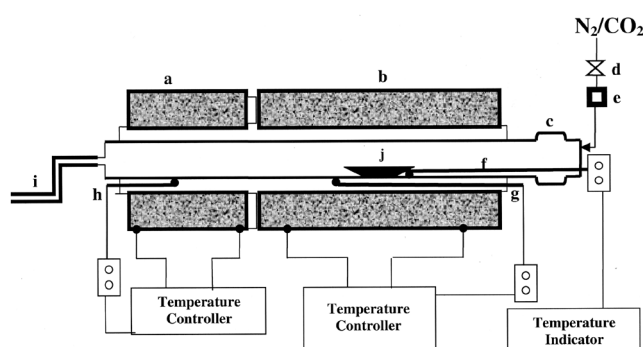
$$r_p = k_p \cdot C_A = \frac{C_A}{1/k_g + R/2De + 1/k_s} \quad (1)$$

Where r_p = rate of physical activation
 k_p = Apparent rate coefficient for physical activation
 C_A = Mass of resin char
 k_g = Mass transfer Coefficient between fluid and particle
 R = Radius of unreacted particle
 De = Effective diffusion coefficient of gaseous reactant in the ash layer
 k_s = Surface reaction coefficient

The resistances described in equation (1) should govern the physical activation. However during physical activation of polymeric resin chars, the ash layer resistance described by $R/2De$ in equation (1) does not exist due to absence of any inorganic impurity or catalyst. Since the reacting gas CO₂ is coming from the surrounding atmosphere given by the cylinder at a definite flow, the gas film resistance k_g is present. The surface reaction resistance k_s will also be operative, as it is the reaction between solid char and gas. Therefore equation (1) reduces to:

$$r_p = k_{papp} \cdot C_A = \frac{C_A}{1/k_g + 1/K_s} \quad (2)$$

The differential method of analysis was used to determine the parameters of rate equation of both PFR1 and CFR1 resin chars. Fig. 2 is a representative plot between percent conversion vs time. Slopes of these graphs give the rate of reaction. Rate of reaction against change in mass is plotted as Fig. 3a, b and c at temperatures 850, 950 and 1000°C respectively. It is clear from the graph that in the temperature range 850 to 1000°C the order of reaction for PFR1 resin



a = furnace 1, b = furnace 2, c = quartz tube, d = needle valve, e = flow meter, f, g, h = thermocouples, i = outlet to sink, j = silver boat

Fig. 1. Experimental Setup.

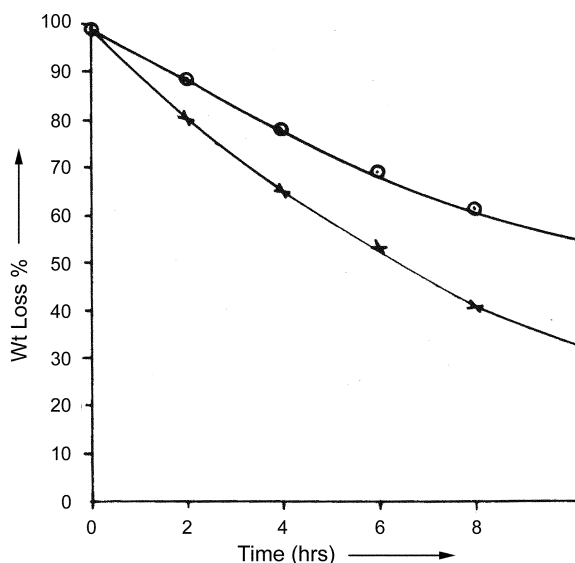


Fig. 2. Conversion Vs time plot of physically activated resins (T=1000°C).

char is first order. However, in case of CFR₁ resin char the rate of reaction follows the first order reaction kinetics upto 950°C temperature and on going to 1000°C the rate of reaction appears absolutely independent of the reactant resin char mass and thus the order of reaction is zero order. In the solid gas reactions the rate of reaction will also be affected by the surface area of solid available for the interaction of gas. In the present study, since the reacting solid is porous, it is important to get knowledge about the external surface area available for the interaction of gas. The external surface area of each of the sample was evaluated by α_s method [4]. A standard nonporous material, hydroxylated silica in our case, was taken as reference for this purpose. The N₂ adsorption isotherm data at 77 K of reference sample was utilized to get the normalized adsorption i.e. α_s values at 0.001~0.90 relative pressure range. The volume adsorbed at a known relative pressure (obtained from N₂ adsorption isotherm) of each sample was plotted against the α_s values at that particular pressure. Graphs shown in Fig. 4. External surface area was calculated by dividing the slope of test sample by slope of reference sample multiplied by surface area of standard reference sample. Rate of reaction and external surface area data is given in Table 1. It is seen that the external surface area of PFR₁ resin char is almost constant from 850~1000°C reflecting that imperfections i.e. cracks, crevices, and voids having width larger than depth which constitute the external surface area are not created easily, in spite of that there is an increase in the total surface area from 701~1050 m²/g. This leads to the conclusion that in this particular resin char matrix, new pores are formed which contribute to creation of internal surface rather than external surface. This might have happened due to preferential burning of soot, which hitherto blocked these pores. The rate of reaction in this case first

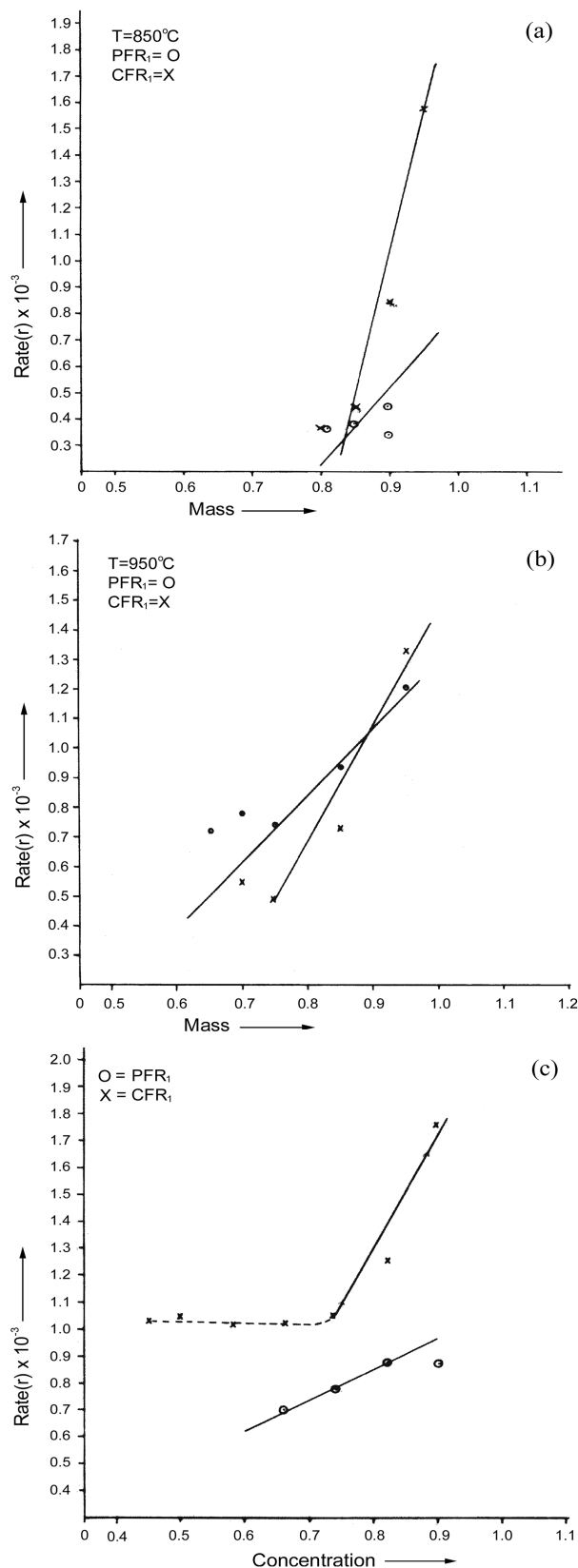


Fig. 3. a, b, and c showing dependency of rate of reaction with change in mass from 850 to 1000°C.

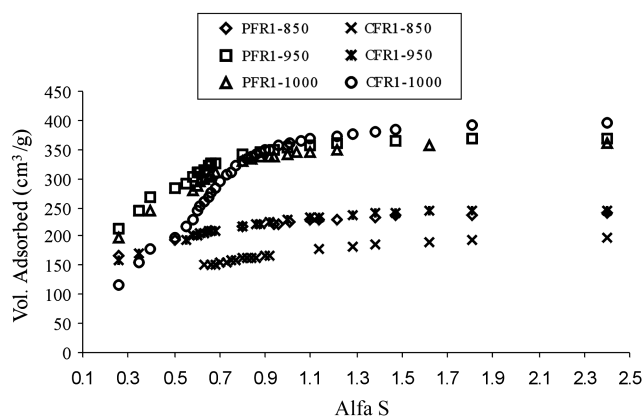

 Fig. 4. α_s plot of physically activated samples.

Table 1.

Sample	Temperature (°C)	Ext. Surface Area (m ² /g)	Rate of reaction (g/min.)	Total Surface Area (m ² /g)
PFR1	850	36.77	0.37×10^{-3}	701
PFR1	950	34.55	0.67×10^{-3}	1084
PFR1	1000	31.26	0.58×10^{-3}	1050
CFR1	850	38.29	0.25×10^{-3}	503
CFR1	950	29.02	0.65×10^{-3}	685
CFR1	1000	55.73	0.78×10^{-3}	1119

increases marginally on going from 850 to 950°C, but levels off on further raising the temperature to 1000°C. In case of CFR1 resin a continuing rising trend in rate constant values is observed. However, the rise in rate of reaction in both cases are not significant and this may be due to gas film resistance which is perhaps a boon and curse at the same time. The gas film resistance makes the process more energy intensive but regulates the burn off and helps in creation of porosity in the desired range to give large surface area. In the case of CFR1 resin char, an increase in the external surface area from 38~56 m²/g with temperature is observed. Rate of reaction also increases from 0.25×10^{-3} – 0.78×10^{-3} g min⁻¹ with increase in external surface area. This is also associated with considerable increase in total surface area from 503~1119 m²/g in CFR1 resin system.

The apparent rate constants of physical activation at

Table 2.

Temperature (°C)	Rate Constant (min ⁻¹)		Mechanical Strength (g/Particle)	
	PFR1	CFR1	PFR1	CFR1
850	3.8×10^{-3}	3.41×10^{-3}	460	150
950	7.58×10^{-3}	5.22×10^{-3}	306	112
1000	7.94×10^{-3}	10.9×10^{-3}	379	49

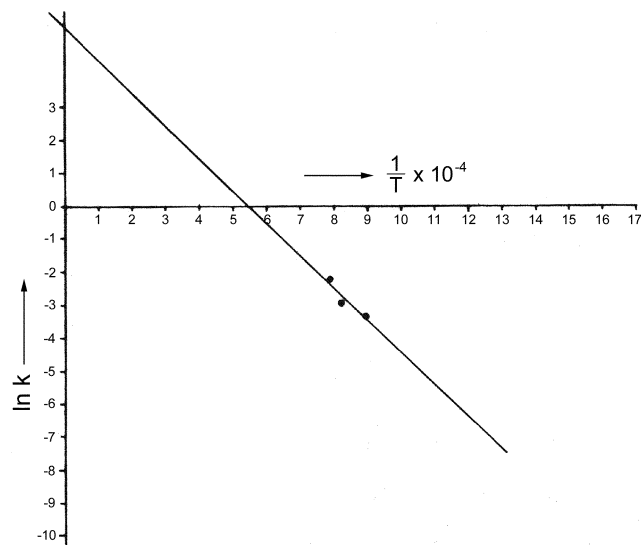


Fig. 5. Arrhenius plot of physically activated CFR1 resin.

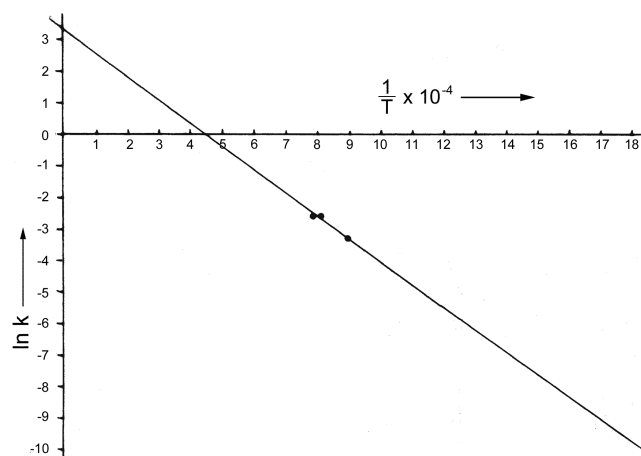


Fig. 6. Arrhenius plot of physically activated PFR1 resin.

different temperatures were calculated assuming pseudo first order kinetics and are given in Table 2.

Figs. 5 and 6 are the Arrhenius plots for CFR1 and PFR1 resin chars respectively. The energies of activation of PFR1 and CFR1 resins calculated from the Arrhenius plots are 1.4×10^4 and 1.98×10^4 cal./g mol. respectively. The complete rate equation for physical activation of PFR1 resin char is:

$$r_{\text{PFR1}} = 27.11 e^{-14000/RT} C_{\text{PFR1}}$$

Complete rate equation for CFR1 resin char is:

$$r_{\text{CFR1}} = 210.60 e^{-19800/RT} C_{\text{CFR1}}$$

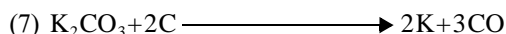
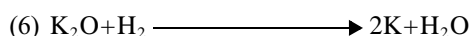
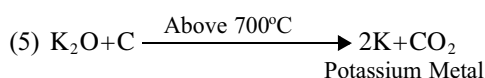
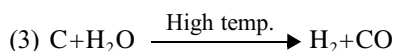
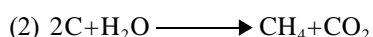
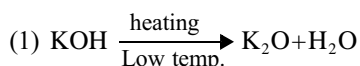
Test for the mechanical strength evaluation was performed using standard ASTM C-695 & E-4 method, given in table 2. Particle size taken was 0.6~0.71 mm for the test. It has been observed that activated carbon obtained from PFR1 resin char bears better strength (i.e. 460~306 g/particle) than

CFR1 resin char (i.e. 150~49 g/particle) after 8hr activation in the temperature range 850~1000°C, due to the close packed arrangement of aromatic units in PFR1 resin system.

3.2. Kinetics of Chemical Activation:

Using KOH as activating agent at 750°C for 30~120 minutes chemically activated both PFR1 and CFR1 resin chars. The activated carbon samples obtained were characterized for surface properties, which were found better in case of CFR1 resin system. Therefore CFR1 resin chars were selected for further kinetic studies. In chemical activation process, reactants are solid carbon, CO₂ gas and steam as obtained on the decomposition of KOH heated in the presence of N₂. The potassium hydroxide is taken in the large excess i.e. four times to the resin chars. The excess of KOH ensures the maximum activation as the reaction of KOH with char is stoichiometric rather than catalytic [5]. Since the KOH taken is in large excess the dependency of rate of reaction on the concentration of KOH has been omitted.

Possible reactions in chemical activation process are: [6, 7]



The difficulty in the solid phase kinetics is the number of variables that need to be taken into account. In the present case the temperature variation is minimized by passing N₂ within ±1°C. The bed height is very small hence pressure drop is considered to be negligible. In gas solid reaction the concentration of reactant gas decreases in longitudinal direction. However, in this case the activating gas liberates at the solid phase itself. Hence the variation in concentration of activating gas is also neglected. If the reacting gas is coming from surrounding atmosphere, it has to diffuse across the buffer zone created by the reaction products around the resin chars i.e. gas film resistance. However, in our case the gas film resistance is absent because the activating gas liberates at carbon site only due to the presence of KOH. Hence the rate equation for chemical activation can be given by:

$$r_c = \frac{C_A}{R/2De + 1/k_s} \quad (3)$$

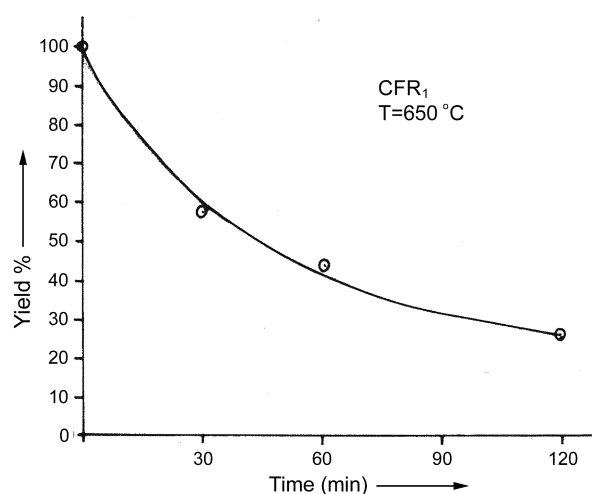


Fig. 7. A representative graph showing wt. loss with time during chemical activation of CFR1 resins.

Where r_c = rate of chemical activation

Since the activation reaction takes place on the solid chars surface therefore, the surface reaction resistance k_s should be operative. If there are impurities present in chars ash layer formation may take place constituting the ash layer resistance. In chemical activation method, potassium hydroxide is used in excess, which activates carbon and transforms into K₂CO₃ which further decomposes to metallic potassium and oxides of carbon [8, 9]. Due to the presence of inorganic species, ash layer formed leads to ash layer resistance represented by $R/2De$ in equation (3). Similar to the physical activation

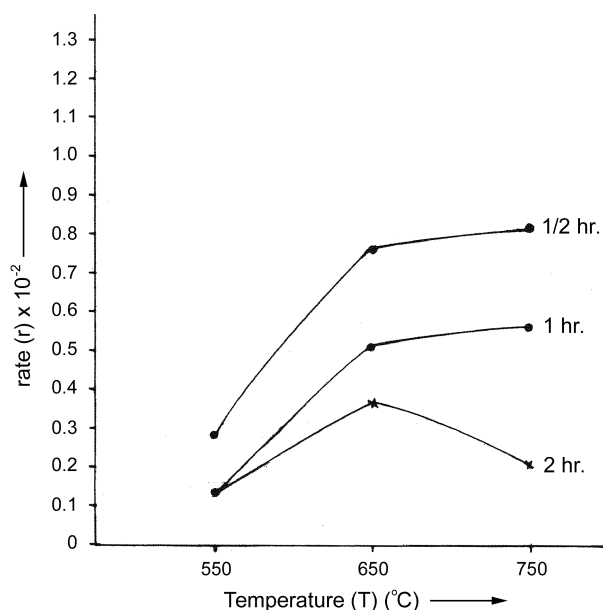
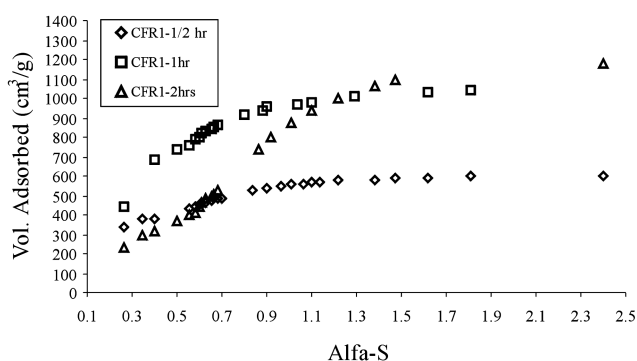


Fig. 8. Graph showing change in rate of reaction with temperature for 30, 60, and 120 min activation time in chemical activation method.

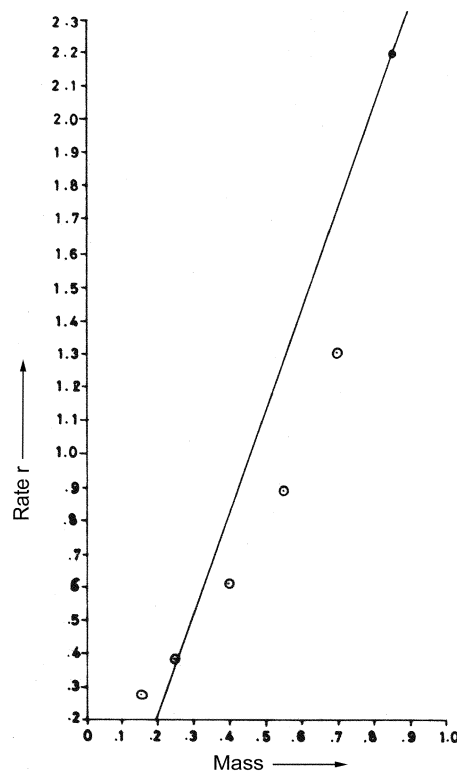
Table 3. (CFR1)

Time (min)	Ext. Surface Area (m ² /g)	Rate of reaction (g/min)	Total Surface Area (m ² /g)
30	106.66	0.816×10^{-2}	1745
60	190.0	0.563×10^{-2}	2895
120	602.45	0.210×10^{-2}	2505

**Fig. 9.** α_s plot of chemically activated samples.

method differential method of analysis has been used to determine the parameters of rate equation. The yield vs time was plotted at different temperatures i.e. 550–750°C. A representative graph (at 650 °C) is shown in Fig. 7. The rate of reaction at different time intervals was calculated from the slope of above graphs and plotted in Fig. 8. It is observed from the curve that the temperature sensitivity decreases with increase of activation duration. Beyond 1h activation the rate of reaction decreased considerably on going from 650 to 750°C. This may be due to the fact that with increasing time the material becomes highly porous and the activating gas molecules have to diffuse through fine pores to reach the reactive sites, and the rate of reaction in fine pores may be governed by Knudsen Diffusion. For the sample activated at 750°C N₂ adsorption isotherm was measured at 77 K using Sorptomatic Surface Area Analyser. The surface properties using BET and as method are shown in Table 3 and Fig. 9. We observe a gradual increase in external surface area (i.e. 107~190 m²/g) and in internal surface area upto 1hr activation time, beyond that (after 2hr activation) there is a tremendous increase in external surface area i.e. from 190.00 to 602.45 m²/g, but a marginal decrease in total surface area was observed. This may be due to the widening of pores after 2hr activation time and these pores now may be considered as outer surface. It is also obvious from the Fig. 9 that pores are present in meso and macro pore range along with micropores in the sample activated for 2 hrs, as there is much more deviation in the α_s plot of this particular sample from standard nonporous sample.

Taking into consideration pore diffusion, the rate equation (3) can be written as:

**Fig. 10.** Change in rate with reactant mass.**Table 4.**

Temperature (°C)	Rate constant (min ⁻¹)
550	1.29×10^{-2}
650	2.42×10^{-2}
750	3.00×10^{-2}

$$r_c = k_{c,app} \cdot C_A = \frac{1}{R/2Re + 1/k_s + 1/k_i} \cdot C_A \quad (4)$$

Where $k_{c,app}$ = apparent rate constant for chemical activation
 k_i = pore diffusion coefficient

The apparent rate constants of activation at different temperatures calculated assuming pseudo first order kinetics are given in Fig. 10 & Table 4. The Arrhenius plot from these values is shown in Fig. 11. The energy of activation calculated from Arrhenius plot is 6.890×10^3 cal/g. mole which is almost one third of the value obtained in case of physical activation. The complete rate equation for chemical activation of CFR1 resin char as determined is

$$r_c = 1.26 e^{-6890/RT} \cdot C_A$$

Higher rate of reaction and lower activation energy observed in case of chemical activation may be due to catalytic effect of metallic potassium obtained as a reaction product.

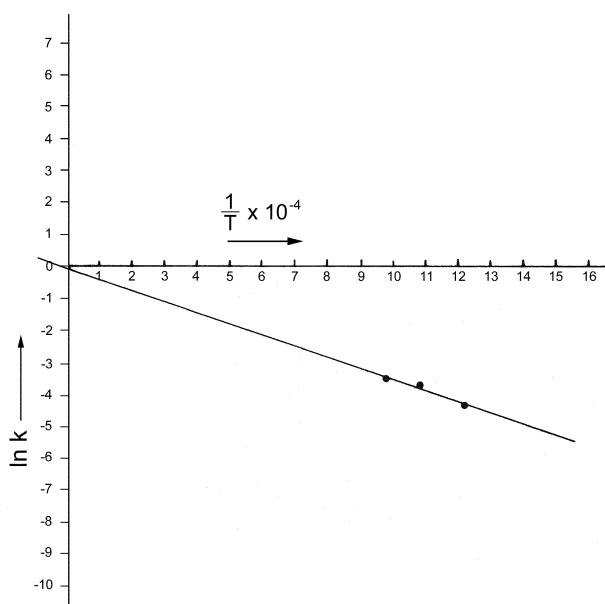


Fig. 11. Arrhenius plot of chemically activated CFR1 resin.

4. Conclusion

Porous carbons from phenolic resins were prepared by physical as well as chemical activation technique. An attempt has been made to evaluate the kinetics of activation of phenolic resin chars. It seems from the study that the temperature dependency of reaction rates for PFR1 and CFR1 resin chars is quite different during physical activation. Shifts in the order of reaction were also noted with temperature and type of precursor resin. With increasing temperature CFR1 resin showed remarkable increase in reaction rate and external surface area, whereas, PFR1 resin showed a gradual increase in reaction rate upto 950°C, beyond that reaction rate decreases. An increase in total surface area upto 950°C and slight decrease in external surface area upto 1000°C was noticed in case of PFR1 resin char leading to the conclusion that new pores are formed in the micropore region upto 950°C without pore widening. From the above results it can also be concluded that imperfections are created more easily in CFR1 resin char than PFR1 resin char at higher temperature. Kinetic study

shows that the CFR1 resin char can be chemically activated at much lower temperature than physical activation as it is obvious from the rate equation that the activation energy drops sharply (i.e. from 19800 to 6890 cal/g. mole) as we go to chemical activation. The rate of reaction for chemical activation is 10 times faster than physical activation requiring shorter duration and lower temperature for activation, which ultimately save the energy. One of the interesting feature noticed, in the sample activated chemically for 2 hrs, is the presence of very high percentage of external surface area which can be utilized for the adsorption of bigger molecules, such as bacteria or other toxic chemical agents. This can be attributed to the fact that KOH dissociates to metallic potassium above 700°C and intercalates into the carbon matrix, which has a catalytic action. After washing the intercalated potassium leaves the carbon matrix in the form of KOH.

References

- [1] Sabri Ergun; Morris Mentser, Chemistry & Physics of Carbon, Volume 1, p. 204-205.
- [2] Damyanti Agarwal; Tripathi, V. S.; Mathur, G. N. proceeding of symposium on polymers and composites, Macro 2000, **2000**, 715-719.
- [3] Shen, J.; Smith, J. M. *Ind Eng. Chem. Fundamentals* **1965**, 4, 293.
- [4] Carruthers, J. D.; Cutting, P. A.; Day, R. E.; Harris, M. R.; Mitchell, S. A.; Sing, K. S. W. *Chem. and Ind.* **1968**, 1772; Bhambhani, M. R.; Cutting, P. A.; Sing, K. S. W.; Turk, D. H. *J. Colloid Interface Sci.* **1972**, 38, 109.
- [5] Delannay, F.; Tysoe, W. T.; Heinemann, H.; Sonorjai, G. A. *Carbon* **1984**, 22(4), 401-407.
- [6] Otawam, T.; Nagima, Y.; Miyazaki, T. *Carbon* **1997**, 35(9), 1315-1319.
- [7] Kapteijn, F.; Jurriens, J.; Mouliyin, J. A. *Fuel* **1983**, 62, 249.
- [8] Otawa, T.; Tanibata, R.; Itoh, M. *Gas separation and purification* **1993**, 7, 241.
- [9] Otawa, T.; Naima, Y.; Itoh, M. *Proceedings of the 5th International Conference on fundamentals of adsorption*, Pacific Grove, May 1995, 13-18.