

Influence of Pyrolysis Temperature on the Adsorptive Properties of Adsorbents Produced from Novolac and Biomass

J. SFYRAKIS, A. FALIAGAS, and J. SIMITZIS*

National Technical University of Athens, Department of Chemical Engineering, Laboratory of Special Chemical Technology, 9 Heron Polytechniou str., Zografou Campus, GR-157 80 Athens, Greece

SYNOPSIS

Mixtures of novolac resin and olive stone biomass are cured and pyrolyzed at different temperatures to yield carbonaceous adsorbents. The weight losses and the shrinkages taking place in the carbonization process increase up to ca. 600°C. The pyrolysis residues are investigated with respect to their ability to adsorb toluene and cyclohexane from the vapor phase. Toluene is adsorbed on all adsorbents stronger than cyclohexane. The overall diffusion coefficient D of the adsorption process, the specific surface area, and the pore volume of the adsorbents are calculated. The adsorptive properties of the products are interpreted taking into account the size and shape of the pores, the polarity of the adsorbate, and the dispersion forces between adsorbent and adsorbate. Slit-shaped pores, which are characteristic of carbon molecular sieves, are likely to be present in the adsorbents which are pyrolyzed at higher temperatures and particularly at 1000°C. This adsorbent shows the highest adsorption concerning the equilibrium uptake, specific surface area, and pore volume of toluene and cyclohexane. However, the diffusion coefficient D is lower as more micropores are present. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Adsorption is an important unit operation for the separation of substances from the liquid or vapor phases. Nowadays, the feasibility of replacing distillation by adsorption, in order to reduce the energy consumption, is pursued. Hybrid processes combining adsorption with distillation are among the more promising approaches for the separation of mixtures, e.g., of propane and propylene.^{1,2} Although common commercial activated carbon has a greater capacity for both propane and propylene than silica gel and molecular sieve 13X, it is only slightly selective for propylene.¹ The use of activated carbon for the removal of toxic organic contaminants, like chlorofluorocarbons and other halocarbons, as well as heavy metals like Cd(II), Hg(II) from aqueous solutions constitutes an interesting research and application field.³⁻⁵

Commercial activated carbons are produced primarily from carbonaceous materials like coals, peat, wood, coconut, and petroleum coke with thermal or chemical activation processes.^{6,7} The demand for activated carbons having modified properties in comparison to common activated carbons led to the development of commercial activated carbons based on the carbonization of typical synthetic polymers, like macroreticular styrene/divinylbenzene copolymers which are used, e.g., in drinking water treatment.^{6,8} On the other hand, natural polymers such as lignocellulosic are nowadays very important as polymeric raw materials combined or not with synthetic polymers like phenolic, epoxy resins, etc.⁹⁻¹² The use of agricultural waste by-products, like peanut hulls, etc., led to the production of low-cost adsorbents.⁵

Polymeric carbon adsorbents have also been produced by using appropriate mixtures of novolac resin (NR) with olive stone biomass (OLB) which is an agricultural by-product produced in very large quantities in mediterranean and other countries.¹³⁻¹⁶

* To whom correspondence should be addressed.

Cured and pyrolyzed composites of NR/OLB with compositions varying from 20/80 to 75/25 NR/OLB exhibited at temperatures up to ca. 600°C, lower weight losses more than expected by the rule of mixtures, due to additional crosslinkages of lignin with hexamethylenetetramine. Such mixtures show differences in their pyrolysis mechanism from what would be expected from the pyrolysis of NR and OLB alone.¹⁷ Furthermore, cured and pyrolyzed composites of NR/OLB = 20/80, as well as other similar mixtures or 100% NR and 100% OLB, adsorb more toluene and cyclohexane from the vapor phase. The aim of this work is to investigate the sorption properties of adsorbents produced by novolac-biomass mixtures in the optimum proportion of 20/80 at different pyrolysis temperatures. The vapor phase adsorption of toluene and cyclohexane will be investigated.

EXPERIMENTAL

Adsorbent Preparation

Carbonaceous adsorbents were produced from novolac resin and biomass in the proportion of 20/80 w/w.^{13,14} The resin was prepared by polymerization of phenol and formaldehyde (in proportion 1.22 : 1 mol/mol) with oxalic acid as catalyst (in proportion 1.5% w/w phenol) after which the resin was sepa-

rated, dried, and pulverized. Biomass consisted of the agricultural/industrial by-product that is left from olives after pressing and separation of the oil. It was dried, ground, and sifted to yield grains with a diameter less than 300 μm . Hexamethylenetetramine (viz., hexa) was used as the curing agent of novolac in proportion 7 : 2 wt novolac/wt hexa. Mixtures of biomass with novolac-hexa were formed as small cylinders after curing at 170°C for 30 min. Carbonization of the cured specimens was accomplished in a cylindrical tube oven under the continuous flow of N_2 . The oven was heated at different temperatures (between 500 and 1000°C) at the rate of 4°C/min, after which the samples remained in the oven for a further 10 min and subsequently cooled to room temperature and kept under vacuum.

Characterization by Sorption

The adsorbents produced by carbonization of the cured material were degassed prior to use under vacuum at 200°C for 3 h. Toluene and cyclohexane, used for the vapor phase adsorption, were reagent grade. For the vapor phase adsorption experiments a quartz spring apparatus including a Griffin and George cathetometer was used. This apparatus is described in detail in Refs. 18 and 19. All sorption experiments were conducted at 20°C and 0.1 pressure relative to the saturation pressure of the vapor

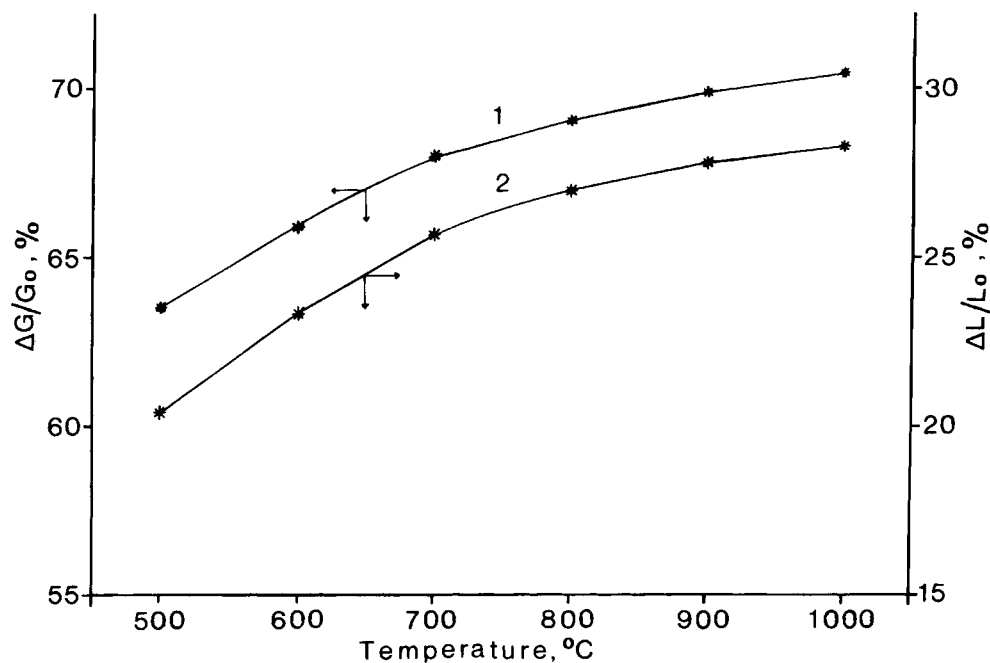


Figure 1 Weight loss (1) and shrinkage (2) vs. novolac contained in the initial mixture: (ΔG) weight loss, (G_0) initial weight, (ΔL) shrinkage, (L_0) initial length.

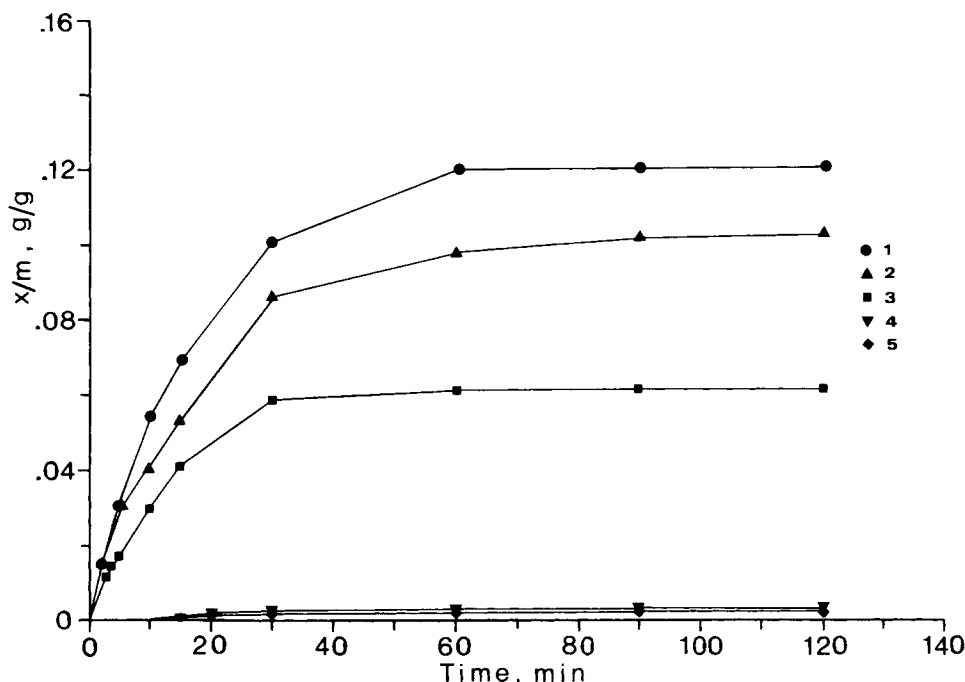


Figure 2 Adsorption of toluene vs. time: x , adsorbed amount of vapor and m , amount of carbonaceous adsorbent. (1) 1000°C, (2) 900°C, (3) 800°C, (4) 600°C, and (5) 500°C.

at this temperature. It is a common practice to determine micropore volumes at relative pressures in the range 0.01 to 0.2.^{20,21}

RESULTS

Figure 1 shows the weight losses and shrinkages of the materials during the carbonization process up to 1000°C. It is observed that they increase with increasing pyrolysis temperature and especially up to 600°C. The plots of the change in weight and length versus pyrolysis temperature follow almost parallel curves.

Figures 2 and 3 show the weight of the adsorbed vapor (toluene and cyclohexane, respectively) per unit weight of adsorbate (viz., uptake) versus time, for the adsorbents pyrolyzed at different temperatures. The curves show initially a strong increase up to about $t = 30$ min, after which they are gradually stabilized at about $t = 60$ min. The behavior of all adsorbents against both adsorbates toluene and cyclohexane is qualitatively similar. Both toluene and cyclohexane are slightly adsorbed on the adsorbents pyrolyzed up to 600°C. The adsorption of toluene is remarkably higher than that of cyclohexane for the corresponding adsorbents pyrolyzed above 800°C.

If the particles can be approximated as uniformly

porous spherical bodies of fixed size, then diffusion theory shows that diffusion controlled uptake into an initially empty solid from a gas phase at fixed pressure can be approximated at small times by the equation:^{22,23}

$$\frac{Q_t - Q_0}{Q_\infty - Q_0} = \frac{6}{\sqrt{\pi}} \left(\frac{Dt}{a^2} \right)^{1/2} \quad (1)$$

where Q_t , Q_0 , Q_∞ are the amounts adsorbed at time t , when $t = 0$, and at equilibrium ($t > \infty$), respectively. D is the diffusion coefficient, assumed to be independent of concentration, and a is the effective radius of the particle.

The calculation of D depends on parameter a which is difficult to determine. Different considerations concerning the type and the values of parameter a have been reported in the literature. In many cases of carbonaceous adsorbents, parameter a can be set equal to the particle radius r .²³⁻²⁵

Figures 4 and 5 show the ratio of the vapor uptake at time t divided by the corresponding equilibrium value, against the square root of the time. Similar behavior is observed in the adsorption of both toluene and cyclohexane. The quantity D/a^2 can be calculated by the initial slopes of the curves of Figures 4 and 5.²³ Then, the diffusion coefficients D are calculated by using the above equation considering

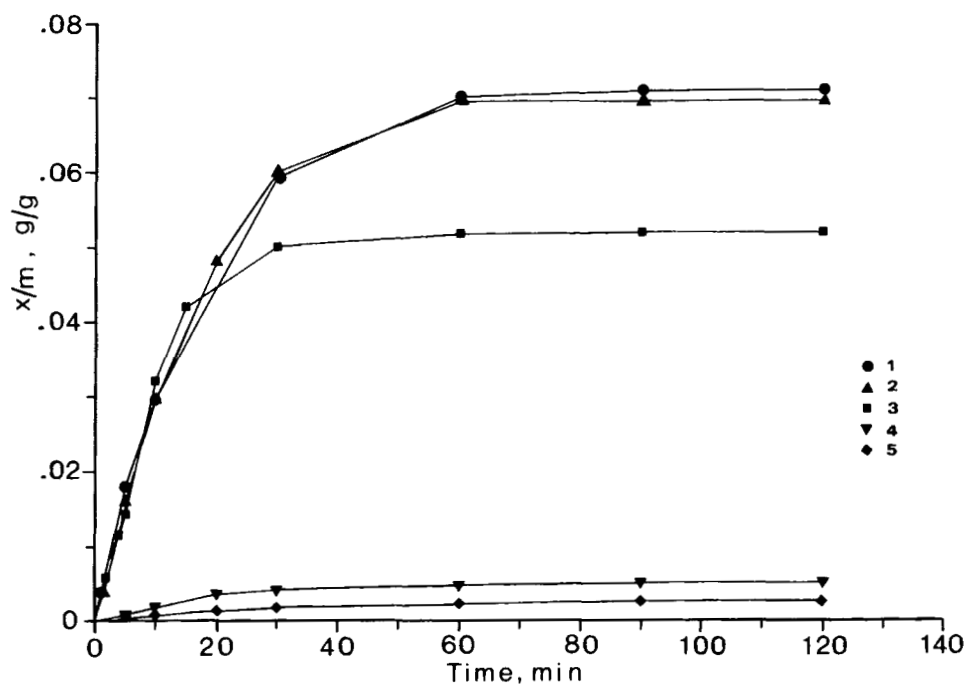


Figure 3 Adsorption of cyclohexane vs. time: x , adsorbed amount of vapor and m , amount of carbonaceous adsorbent. (1) 1000°C, (2) 900°C, (3) 800°C, (4) 600°C, and (5) 500°C.

the particle radius r in place of the parameter a . The particle radius r is the radius of a sphere having equal external surface to that of the cylindrical

samples used. The calculated values of D/a^2 and D are given in Table I. From the plot of D versus pyrolysis temperature T (Fig. 6), three ranges can be

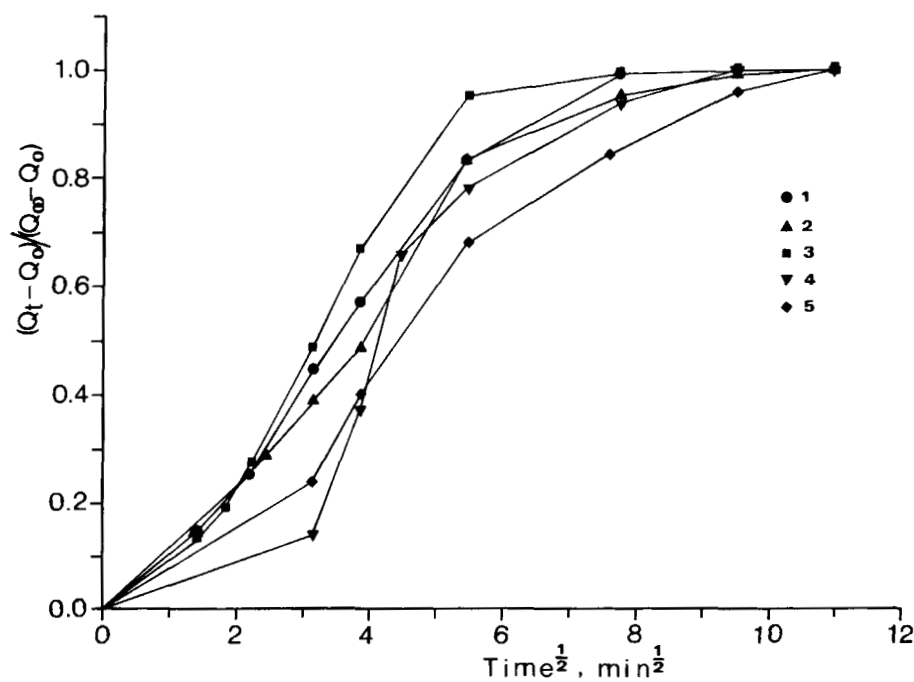


Figure 4 Ratio $(Q_t - Q_0)/(Q_\infty - Q_0)$ vs. the square root of time for the adsorption of toluene. Q_t , Q_0 , Q_∞ = the amounts adsorbed at time t , $t = 0$, and at equilibrium ($t > \infty$), respectively. (1) 1000°C, (2) 900°C, (3) 800°C, (4) 600°C, and (5) 500°C.

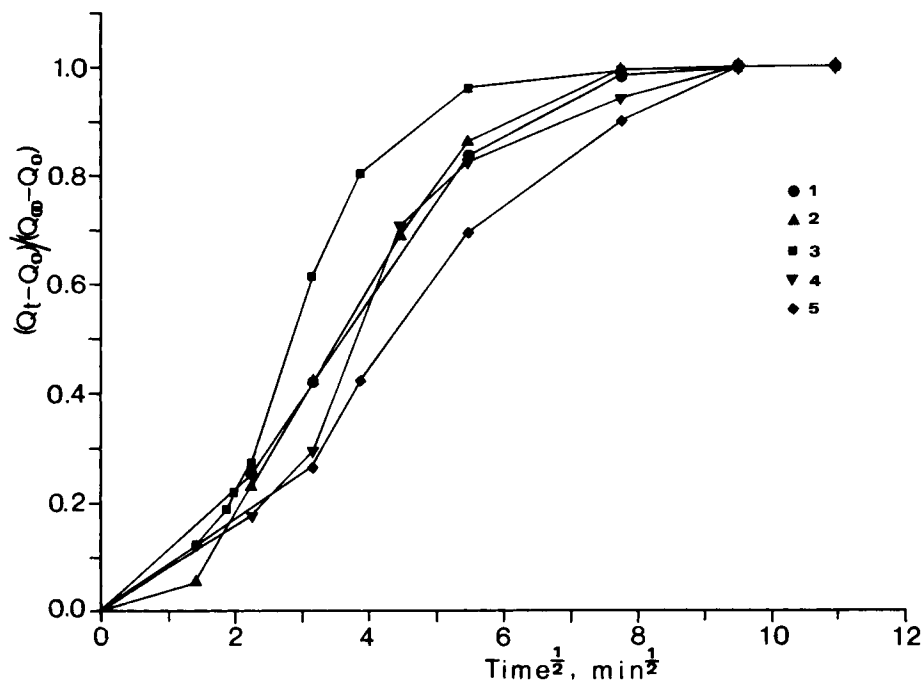


Figure 5 Ratio $(Q_t - Q_0)/(Q_\infty - Q_0)$ vs. the square root of time for the adsorption of cyclohexane. Q_t , Q_0 , Q_∞ = the amounts adsorbed at time t , $t = 0$, and at equilibrium ($t > \infty$), respectively. (1) 1000°C, (2) 900°C, (3) 800°C, (4) 600°C, and (5) 500°C.

distinguished according to the adsorption of toluene: $500^\circ\text{C} < T < 600^\circ\text{C}$, $600^\circ\text{C} < T < 800^\circ\text{C}$, $800^\circ\text{C} < T < 1000^\circ\text{C}$ and according to the adsorption of cyclohexane: $500^\circ\text{C} < T < 800^\circ\text{C}$, $800^\circ\text{C} < T < 900^\circ\text{C}$, $900^\circ\text{C} < T < 1000^\circ\text{C}$. D increases in the first region, then remains almost constant for toluene, and in the third region it decreases. At 1000°C D has the same value for both vapors.

The specific surface area A_p (in m^2/g) can be calculated from the equation:²⁶

$$A_p = (X_m/M)a_m L \times 10^{-20}$$

where X_m is the monolayer capacity in grams of adsorbate per gram of solid obtained from the equilibrium value of adsorption (assuming complete coverage of the monolayer at relative pressure 0.1; Refs. 20 and 21), M is the molecular weight of the adsorbate (i.e., toluene or cyclohexane), a_m is the average area occupied by a molecule of adsorbate in the completed monolayer, and L is the Avogadro

Table I Diffusion Coefficients According to the Diffusion Equation (1)

$T, ^\circ\text{C}$	Vapor	D/a^2 (s^{-1})	Radius a (mm)	D (cm^2/s)
500	Toluene	3.2×10^{-5}	1.2	4.7×10^{-7}
600		3.6×10^{-5}		5.2×10^{-7}
800		3.5×10^{-5}		5.1×10^{-7}
900		3.3×10^{-5}		4.8×10^{-7}
1000		3.1×10^{-5}		4.5×10^{-7}
500	Cyclohexane	3.0×10^{-5}	1.2	4.4×10^{-7}
600		3.2×10^{-5}		4.6×10^{-7}
800		3.3×10^{-5}		4.7×10^{-7}
900		3.4×10^{-5}		4.9×10^{-7}
1000		3.1×10^{-5}		4.5×10^{-7}

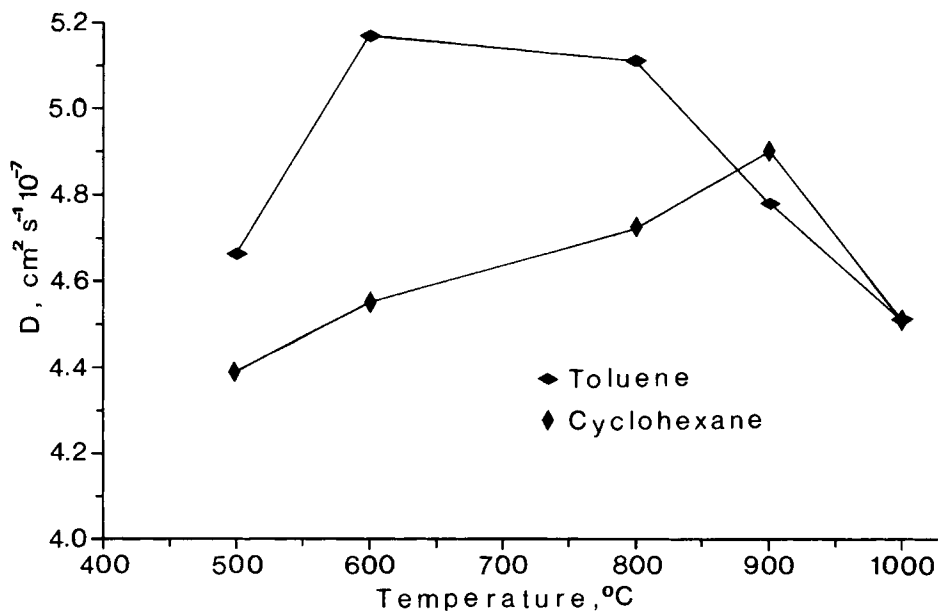


Figure 6 Diffusion coefficient D vs. the pyrolysis temperature T .

constant. According to Ref. 27, the values of a_m are 0.38 nm^2 and 0.46 nm^2 for cyclohexane and toluene, respectively.

Assuming that the volume of adsorbed vapor of the liquid fill up all the pores with diameter greater than the molecular diameter of the adsorbate molecule, then the pore volume (in cm^3/g) can be calculated from the vapor phase adsorption according to the equation:

$$V_p = X_m/\rho$$

where ρ is the density of the adsorbate.

Figures 7 and 8 show the results of the specific surface area A_p and the pore volume V_p for the adsorption of toluene and cyclohexane on the adsorbents. The adsorbent pyrolyzed at 1000°C shows the highest values for A_p and V_p . A very low increase is observed between 500 and 600°C and a strong in-

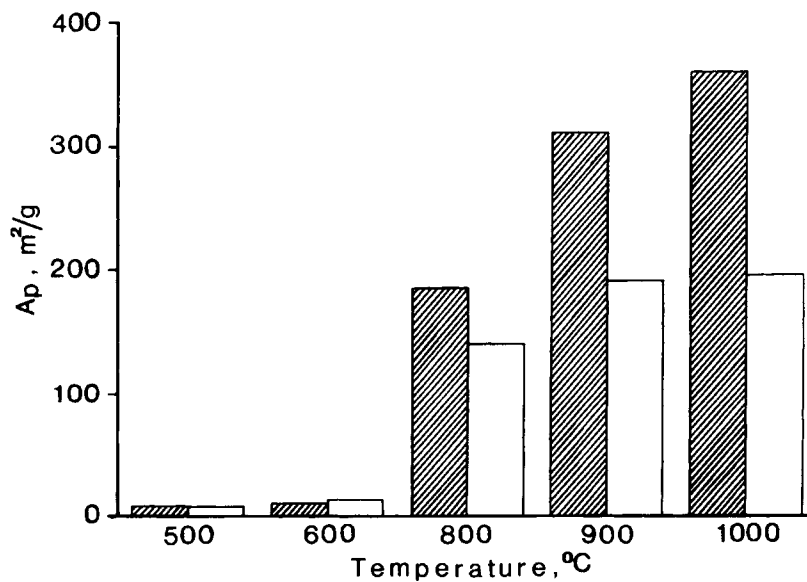


Figure 7 Specific surface area A_p for the adsorption of toluene (shaded) and cyclohexane (blank).

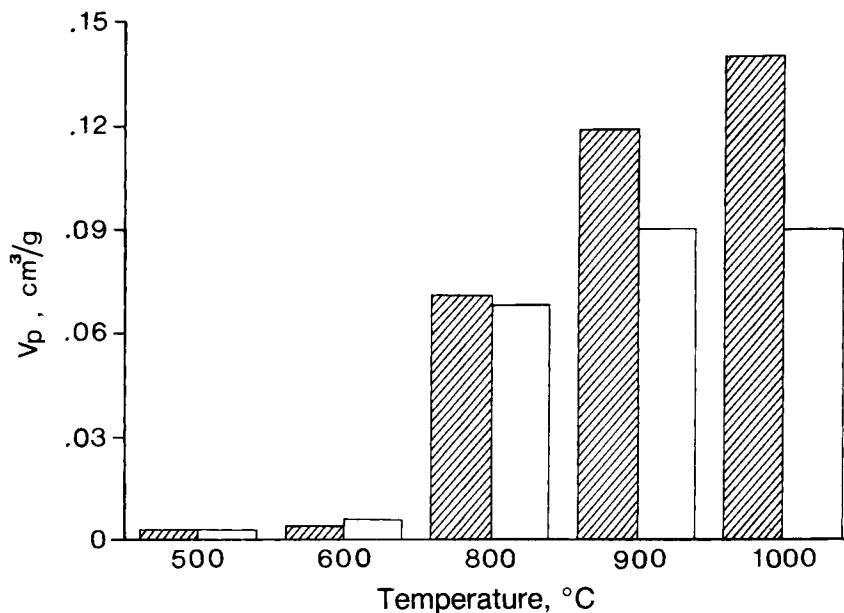


Figure 8 Pore volume V_p for the adsorption of toluene (shaded) and cyclohexane (blank).

crease above 800°C. A_p and V_p are higher for the adsorption of toluene than cyclohexane.

DISCUSSION

It is apparent from Figures 2 and 3 that the relative order of the adsorbents with respect to increasing vapor uptake is in both cases the same:

1. Very low between 500 and 600°C.
2. Intermediate at 800°C.
3. High between 900 and 1000°C.

The carbonaceous residues obtained at different pyrolysis temperatures have different porous structures, which facilitate more or less the adsorption. The adsorbent pyrolyzed at 1000°C seems to have the best porous structure concerning the adsorption of toluene and cyclohexane.

These three regions are in agreement with the results of D (see Fig. 6), particularly for the adsorption of toluene. The higher adsorption rate, equilibrium value (Figs. 2 and 3), and D in uptaking toluene with respect to cyclohexane give evidence that the adsorbent has a selectivity for toluene. The adsorption of an adsorbate on an adsorbent depends on many parameters, such as the pore size of the adsorbent and their distribution, the shape of the pores, the molecular size and the shape of the adsorbate, the polarity of the adsorbent, the adsorbate, etc.

Generally, it is difficult to evaluate the importance of these parameters, and especially for carbonaceous adsorbents which generally, in contrast to other adsorbents like zeolites, do not have a uniform pore structure.

The increase of D for toluene between 500 and 600°C can be explained from the high weight loss (see Fig. 1) which lead to the formation of macropores which facilitate the diffusion. Shrinkage takes place mainly as a geometrical reduction of dimensions of the material leading to the formation of wider pores. Above 800°C the weight loss is very low, as well as the shrinkage. It seems that in this region more micropores are formed. These pores contribute to higher A_p and V_p (Figs. 7 and 8), but the diffusion is hindered and therefore D is lower. The behavior of cyclohexane shows some deviations between 600 and 800°C which can be attributed to its molecular shape (see below).

Concerning the molecular diameters of the adsorbate, the cyclohexane has the value of 4.8×6.8 Å^{7,19} and toluene the value of 6.6 Å.²³ Cyclic compounds, like benzene and cyclohexane which have planar and large molecules, are more suitable to be adsorbed into slit-shaped pores.^{28,29} Carbon molecular sieves prepared by the pyrolysis of polyvinylbenzene, polyfurfuryl alcohol, etc. should have slit-shaped pores which give them their molecular sieve properties.³⁰

The adsorbates used differ not only in their molecular diameter but also in the shape of their mol-

ecules and the polarity. Both toluene and cyclohexane have flat molecules but cyclohexane occurs in two different conformations, i.e., armchair and boat form, the former being more stable.³¹ On the other hand, the dipole moment of the toluene is $1.13 (10^{30} \times p \text{ in Cm})$ and that of the cyclohexane is zero.³² Above about 800°C starts the formation of graphitic ribbon network structures as opposed to the extensive graphitic sheets which must exist in graphitic carbons.³³ The dispersion forces between the aromatic π -electron system of toluene and the π band of the graphitelike planes of the carbon are also responsible for adsorption.³⁴

In conclusion, the adsorbents derived from the mixture of novolac-biomass = 20/80 and pyrolyzed at higher temperatures and particularly at 1000°C seem to contain slit-shaped pores which are characteristic of carbon molecular sieves. Toluene can penetrate into more pores than the cyclohexane for the adsorbents used. The adsorbent pyrolyzed at 1000°C shows the highest adsorption (with respect to equilibrium uptake, specific surface area, and pore volume) for toluene and cyclohexane. However, the diffusion coefficient D is lower as more micropores are present.

REFERENCES

1. T. K. Ghosh, H. D. Lin, and A. L. Hines, *Ind. Eng. Chem. Res.*, **32**, 2390 (1993).
2. H. Jarvelin and J. R. Fair, *Ind. Eng. Chem. Res.*, **32**, 2201 (1993).
3. R. N. Eissmann and M. D. Le Van, *Ind. Eng. Chem. Res.*, **32**, 2752 (1993).
4. J. J. Mahle, L. C. Buettner, and D. K. Friday, *Ind. Eng. Chem. Res.*, **33**, 346 (1994).
5. K. Periasamy and C. Namasivayam, *Ind. Eng. Chem. Res.*, **33**, 317 (1994).
6. P. K. T. Liu, *Ind. Eng. Chem. Res.*, **31**, 2216 (1992).
7. U. Eiden and J. Ciprian, *Chem.-Ing.-Tech.*, **65**(11), 1329 (1993).
8. J. W. Neely and E. G. Isacoff, *Carbonaceous Adsorbents for the Treatment of Ground and Surface Waters*, Marcel Dekker, New York, 1982, pp. 41-51.
9. D. Feldman, D. Banu, A. Natansohn, and J. Wang, *J. Appl. Polym. Sci.*, **42**, 1537 (1991).
10. D. Feldman, D. Banu, C. Luchian, and J. Wang, *J. Appl. Polym. Sci.*, **42**, 1307 (1991).
11. H. Vazquez-Torres, G. Canche-Escamilla, and C. A. Cruz-Ramos, *J. Appl. Polym. Sci.*, **45**, 633 (1992).
12. H. Vazquez-Torres, G. Canche-Escamilla, and C. A. Cruz-Ramos, *J. Appl. Polym. Sci.*, **45**, 645 (1992).
13. J. Simitzis, *Angew. Makromol. Chem.*, **153**, 165 (1987).
14. J. Simitzis and J. Sfyarakis, *Angew. Makromol. Chem.*, **163**, 47 (1988).
15. J. Simitzis and J. Sfyarakis, *J. Anal. & Appl. Pyrol.*, **26**, 37 (1993).
16. J. Simitzis and J. Sfyarakis, *J. Appl. Polym. Sci.*, **54**, 2091 (1994).
17. J. Simitzis, *J. Anal. & Appl. Pyrol.*, to appear.
18. P. L. Walker, Jr. and J. Janov, in *Hydrophobic Surfaces*, F. M. Fowkes, Ed., Academic Press, New York, 1969, p. 108.
19. H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., *Encyclopedia of Polymer Science & Technology*, Wiley-Interscience, New York, 1966, Vol. 5, pp. 72-74.
20. J. Kalka, Ph.D. Thesis, University of Karlsruhe (1970).
21. H. P. Boehm and H. H. Warnecke, *Proceedings of the International Carbon Conference, Carbon 76*, Deutsche Keramische Gesellschaft, Baden-Baden, Germany, 1976, p. 76.
22. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, London, 1968, p. 16.
23. C. G. Pope, *Fuel*, **63**, 1681 (1984).
24. P. L. Walker, Jr., L. G. Austin, and S. P. Nandi, in *Chemistry and Physics of Carbon*, P. L. Walker, Jr., Ed., Marcel Dekker, New York, 1966, Vol. 2, pp. 267-269, 308-310.
25. C. C. Lai and C. S. Tan, *Ind. Eng. Chem. Res.*, **32**, 1717 (1993).
26. S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London, 1982, p. 41.
27. R. S. Mikhail and E. Robens, *Microstructure and Thermal Analysis of Solid Surfaces*, Wiley, New York, 1983, pp. 184, 444, 445.
28. T. G. Lamond, J. E. Metcalff, and P. L. Walker, *Carbon*, **3**, 59 (1965).
29. P. Laudenklos, Ph.D. Thesis, University of Karlsruhe (1975).
30. J. W. Neely and E. G. Isacoff, *Carbonaceous Adsorbents for the Treatment of Ground and Surface Waters*, Marcel Dekker, New York, pp. 41-51.
31. *ABC-Chemie-Fachlexikon*, Verlag Harri Deutsch, Thun, Frankfurt/Main, 1979, Vol. 2, p. 1340.
32. M. D. Lechner, Ed., *Taschenbuch fur Chemiker und Physiker*, Springer-Verlag, Berlin, 1992, pp. 525, 529.
33. G. M. Jenkins and K. Kawamura, *Polymeric Carbons—Carbon Fibre, Glass and Char*, Cambridge University Press, New York, 1976, p. 2.
34. R. W. Coughlin, F. S. Ezra, and R. N. Tan, in *Hydrophobic Surfaces*, F. M. Fowkes, Ed., Academic Press, New York, 1969, p. 44.

Received June 13, 1994

Accepted September 28, 1994