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Removal of benzene from hexane cut by liquid phase adsorption on activated carbon

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Abstract

The present study is aimed at developing a liquid phase adsorption process using activated carbon as adsorbent for removal of benzene from 63-69° hexane cut containing 10,000 ppm benzene to produce petrochemical grade hexane containing 20 ppm benzene. Different activated carbons have been evaluated for this application on the basis of equilibrium adsorption isotherm measurements and column dynamic studies in a fixed bed metallic adsorption column. Steam was used as desorbent. Hexane containing less than 20 ppm benzene could be produced from selected carbons under repeated cycles of adsorption-desorption without any capacity loss. Typical results are presented and discussed.

1. INTRODUCTION

The petrochemical industry requires 63-69°C hexane cut containing 20 ppm benzene and 1 ppm sulphur for use as solvent in polymerisation reactors. This hexane is generally made by catalytic hydrogenation of corresponding naphtha cut. Alternatively this hexane can be produced by liquid-liquid extraction using typical polar solvents like N-methyl pyrrolidone, for example, acid treatment or adsorptive separation with selective adsorbents for benzene like activated carbon or molecular sieves. However, in India, the current demand for this high purity hexane is only 1600 t/a which is being totally imported. This demand is projected to increase to 4000 t/a. For such limited scale of production neither catalytic conversion nor liquid extraction processes would be economic. Acid treatment is also not acceptable due to environmental limitations and moreover it would not be able to meet the stringent specifications for benzene limits in the product. For the present application the adsorptive separation route appears to offer maximum scope for development. Adsorptive separation processes are being successfully used in commercial scale both in bulk separations and purifications in liquid/vapor phase [1]. Their use in liquid phase purification applications (waste water treatment) is largely based on granular activated carbon adsorbents and over a hundred such plants are reported to be operating in the United States alone [2].

2. SCOPE OF STUDY

The present study deals with development of a liquid phase adsorption process for the production of petrochemical grade hexane containing 20 ppm benzene and 1 ppm sulphur from a hexane fraction 63-69°C containing upto 10,000 ppm benzene. The study was aimed at evaluating adsorbents for this application and providing engineering design and scale-up information for design of an adsorption plant for production of 3500 t/a of hexane product. While both granular activated carbon and molecular sieves (13X) are suitable adsorbents for benzene removal from hexane cut, the study was confined to evaluation of activated carbons primarily because of ease of regeneration of spent adsorbent beds with low pressure steam. Molecular sieves require more severe regeneration and drying conditions (250°C). The experimental program drawn up included equilibrium isotherm measurements with selected activated carbon adsorbents, column dynamic studies and bed regeneration studies.

3. EXPERIMENTAL

3.1. Adsorbents Evaluated

Five granular activated carbons were evaluated for their efficacy in removing benzene from hexane by liquid phase adsorption. Their physical characteristics are given in Table 1.

Table 1
Physical characteristics of activated carbons

Carbon	Supplier	Mesh size	Total surface area (m^2/g)	Bulk density (g/ml)	% Pore volume (ml/g)
ICA SP	Industrial Carbons Baroda	20/30 8/16	1000	0.55	
GAC 830	Ato Chem Inc. USA	8/30	950-1000	0.51	0.85
GAC 610	Ato Chem Inc. USA	6/10	900-1000	0.47	0.85
SCG-G	Hyderabad Carbons	20/30 8/16	1200	0.40	1.2
SCG-F	Hyderabad Carbons	20/30 8/16	1050	0.40	0.9

3.2. Equilibrium Isotherm Measurements

Known amounts of activated carbon sample were agitated with refinery hexane feeds containing varying concentrations of benzene for 4 hrs in jacketed flasks maintained at 30°C ± 0.1°C. The equilibrium liquid phase was then sampled and benzene concentration determined by ultra violet spectroscopy as per UOP Method 370-65 [3].

3.3. Adsorption Breakthrough Curve

Raw hexane feed was pumped in an upflow mode through a bed of granular activated carbon kept in a jacketed column. The column was maintained at the desired experimental temperature by circulation of thermostated liquid. Liquid effluent from the top of the adsorption column was periodically sampled and benzene concentration measured by UV spectroscopy. A schematic diagram of the unit is shown in Figure 1. The parameters studied included carbon particle size, bed length, feed flow rate and temperature.

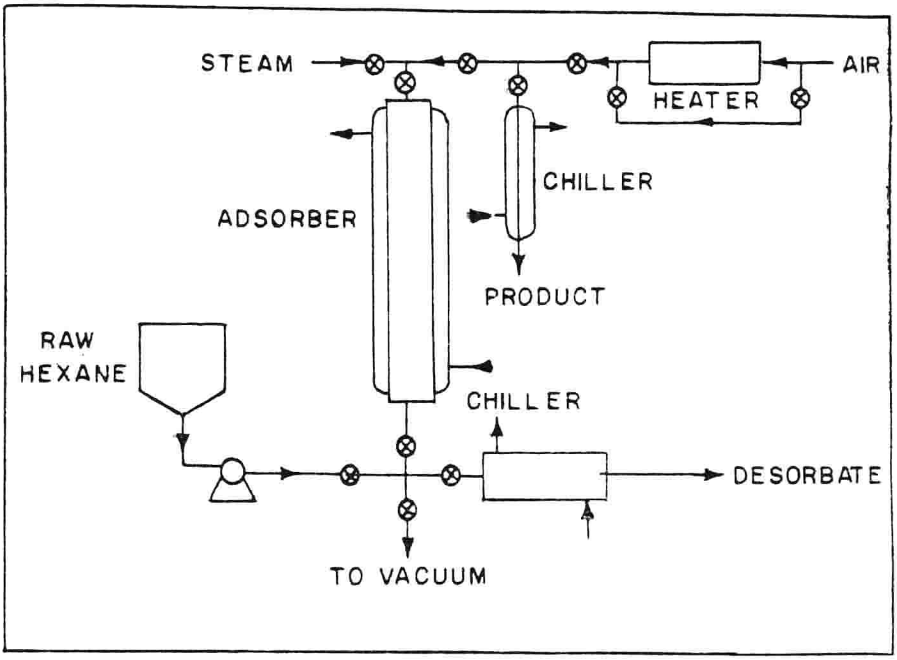

Figure 1. Schematic diagram of liquid phase adsorption unit

3.4. Desorption Breakthrough Curve

The spent adsorbent was regenerated by steam which entered the adsorber from the top, countercurrent to the feed as shown in Figure 1. The desorbed hydrocarbons are condensed in the chiller at the bottom of the column and periodically sampled for benzene concentration measurement. The bed was then dried with hot air or by vacuum, while maintaining bed temperature at 120-130°C by circulation of thermostated liquid. The bed was then cooled by compressed air circulation at ambient temperature. The parameters studied included: steam flow rate and its temperature, air flow rate and its temperature and column pressure.

4. RESULTS AND DISCUSSION

The total adsorption capacity of the activated carbon for benzene could be calculated from the break through concentration-time curve by numerical integration using the relationship.

$$W = F\int_0^\infty (c_o - c)\,dt = F\int_0^{c_o} t\,dc \qquad (1)$$

Of the activated carbons evaluated, four carbons (Table 2)exhibited capacities in excess of 30 mg/g.

Table 2
Total equilibrium capacity for benzene at 30°C
Feed Hexane containing 10,000 ppm benzene

Carbon	Total equilibrium capacity for benzene (mg/g)
Ato Chem GAC 830	50
Industrial Carbon ICA SP	40
Hyderabad Carbon SCG-F	50
Hyderabad Carbon SCG-G	30

In the range of interest (0-10,000 ppm benzene) the equilibrium isotherm is linear. A typical relationship is depicted in Figure 2.

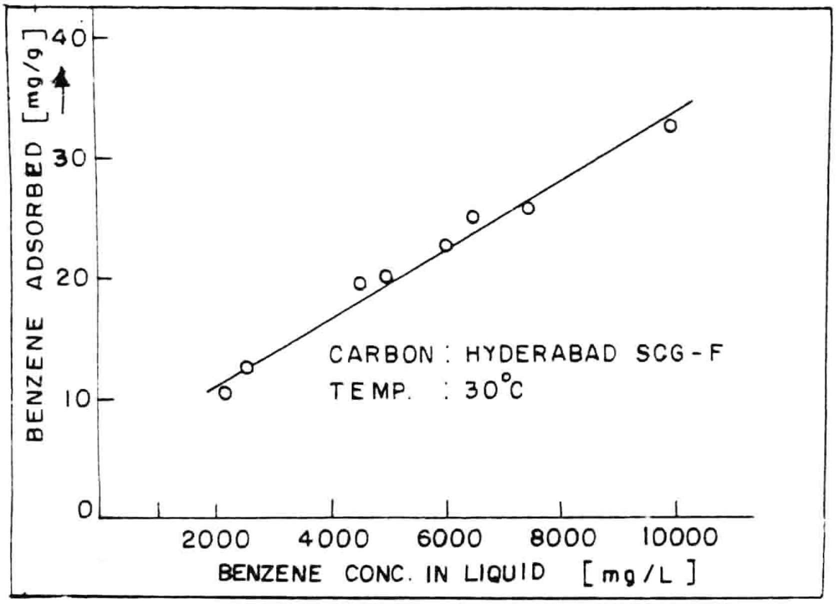

Figure 2. Equilibrium isotherm with carbon SCG-F

From the concentration-time breakthrough curve data obtained with each carbon in the column dynamic studies, the breakthrough time for 20 ppm benzene in the effluent liquid was obtained. This is a critical parameter as it determines the cycle time for the adsorption cycle. The relationship of this breakthrough time and product yield with variation in different operating parameters like feed flow rate, bed height is depicted in Figures 3 and 4 for the activated carbon SCG-F.

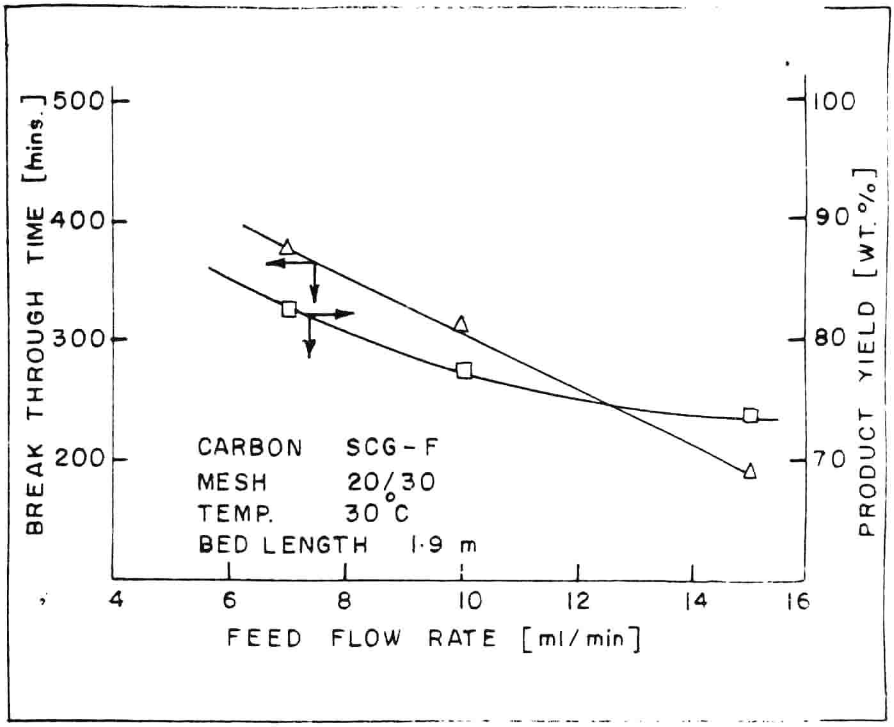

Figure 3. Relationship between feed flow rate and breakthrough time

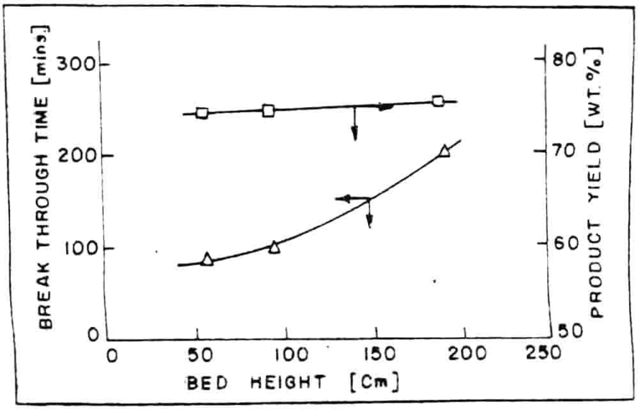

Figure 4. Relationship between bed height and breakthrough point

From these Figures it is evident that both breakthrough time and product yield increase with decrease in feed flow rate. Increasing the bed height also increases the breakthrough time while yield remains almost constant. The breakthrough time and yield decreases as carbon particle size is increased. The increased carbon particle size leads to a more diffuse mass transfer zone because of increased intraparticle diffusional resistance. This is shown in Figure 5.

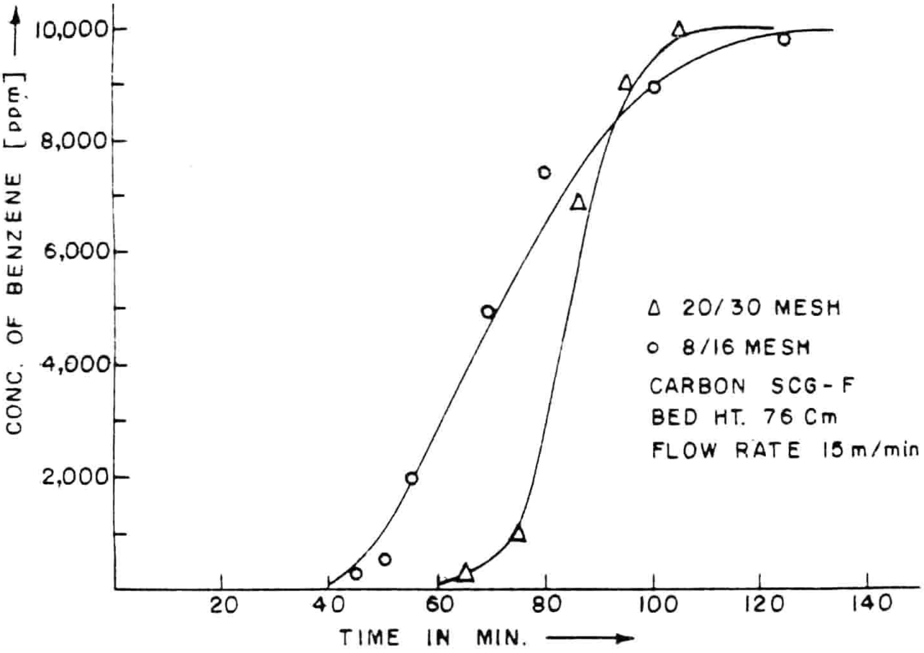

Figure 5. Effect of particle size of carbon on breakthrough curve

The results of these experiments suggest that product yield can be increased by selecting operating conditions so as to increase the breakthrough time. Optimum operating conditions would lie towards low liquid flow rates, small carbon particle size and longer bed lengths.

Experiments on steam desorption of the spent adsorbent bed indicate that over 85% of the adsorbed hydrocarbons and void liquid in the bed are stripped off by low pressure steam within the first 10 minutes of the process. Significant "tailing" of the desorption curve is then observed and the time required to complete the desorption depends significantly on steam rate. This is shown in Figure 6.

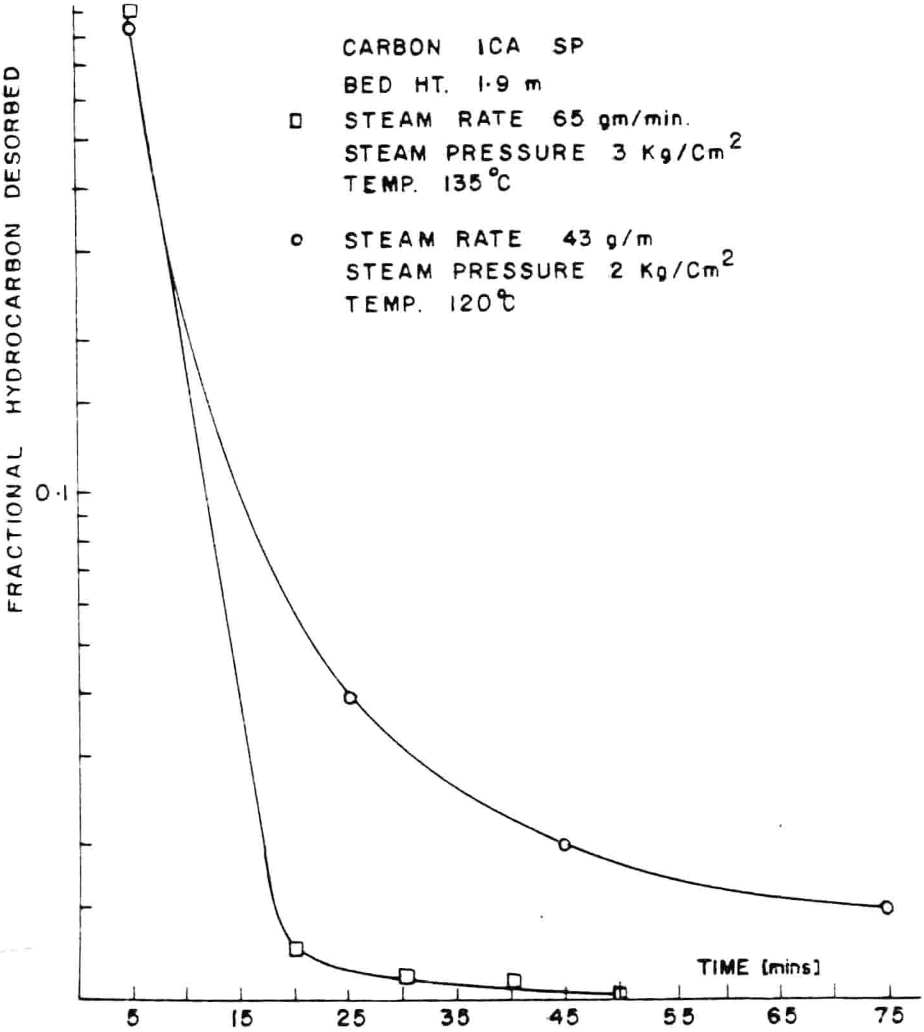

Figure 6. Effect of steam rate on desorption

For a typical granular activated carbon the steam requirement for desorbing the total organics in these experiments works out to be around 12 lb/lb desorbate.

After the steam desorption step the bed drying was studied. The bed drying studies involved use of hot air at temperatures 120-130°C and flow rates 50 to 100 l/min. Alternatively use of vacuum to dry the bed was also studied.

It was observed that breakthrough time and hence product yield are also influenced by the bed drying procedure used. The use of vacuum (150-200 mm Hg) drying while maintaining the bed at around 120°C by hot oil circulation through the adsorber jacket gave a 5% increase in product yield compared to hot air drying. The drying period was around 1 hr in both cases.

The bed was then cooled by using compressed air at ambient temperatures and the cycle of experiments repeated.

The selected carbon SCG-F was found to perform satisfactorily in giving around 75% product yield over repeated cycles of adsorption and desorption.

For this particular carbon the optimum operating cycles are given below.

Adsorption	210 mins
Column drain	30 mins
Steam desorption	60 mins
Vacuum drying	60 mins
Air cooling	60 mins

Based on the results of this study a commercial plant of 3500 t/a capacity for production of petrochemical grade hexane is being built at Bombay in India. A diagram of the flow sheet for this plant is given below.

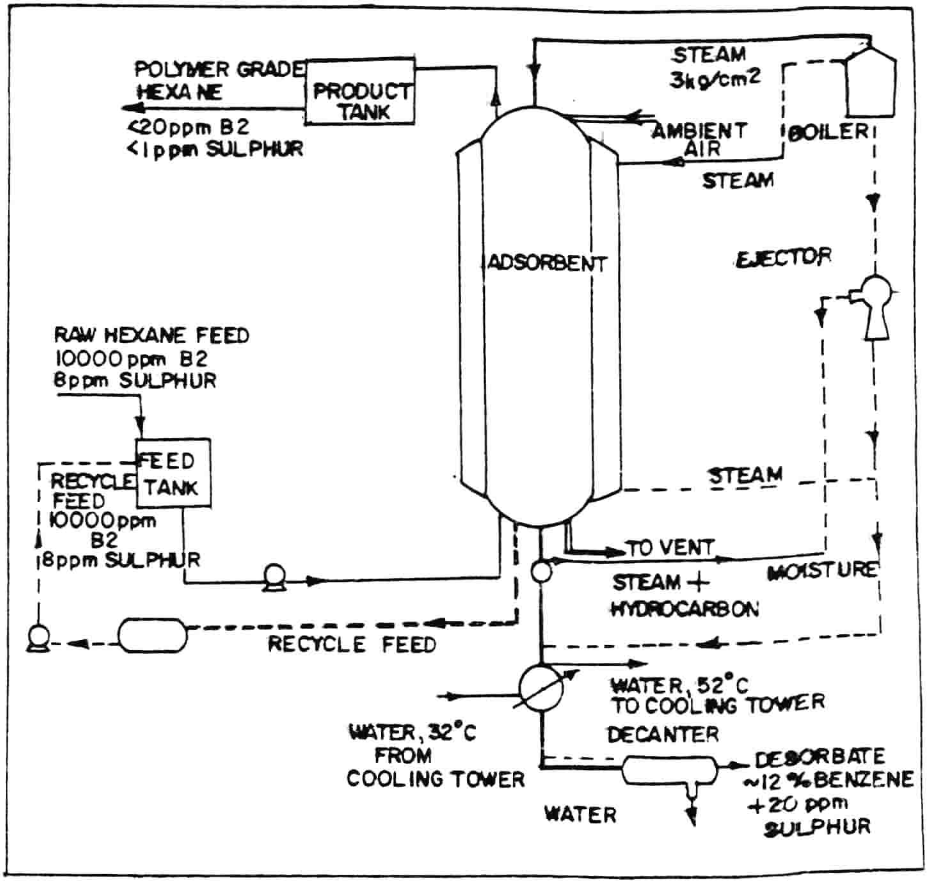

Figure 6 Schematic diagram of process flowsheet.

5. CONCLUSIONS

In conclusion we note that

i) Benzene from refinery hexane 63-69°C cut can be removed to below 20 ppm by liquid phase adsorption on granular activated carbon at ambient temperature (30-35°C).

ii) The treated hexane meets specifications for petrochemical grade hexane.

iii) The spent carbon can be regenerated by low pressure steam followe by vacuum drying and cooling with air.

iv) Product yield of around 75% is maintained through repeated cycles of adsorption-desorption. Bed performance does not deteriorate.

v) The process will generate a by-product stream of hexane containin around 12%-15% benzene which can form gasoline blending stock.

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REFERENCES

1. D.M. Ruthven. Chem. Eng. Progress 84, Feb 1988, 42

2. P.N. Cheremisinoff and E.F. Gonsalves
Principles and applications of Carbon Adsorption. Handbook of Heat & Man Transfer Vol 2, 1211 Gulf Publisher Co. Houston 1986.

3. Laboratory Test Methods for Petroleum and its Products.
UOP Process Division Des Plaines, Illinois 1982.

NOMENCLATURE

C : Concentration, mg/L.

F : Flow rate ml/min.

t : Time mins.

W : Amount adsorbed mg/gm.

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Adsorption equilibria for binary mixtures of nonelectrolytes on chemically modified surface of active carbons

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Abstract

The adsorption selectivity of active carbons depends strongly on the chemical composition of their surface. A significant role is here ascribed to the surface oxygen functional groups. The measurements of adsorption from binary liquid mixtures containing polar and nonpolar component are useful to determine the chemical character of the surface of modified carbon materials [1-3]. The range of preferential adsorption of these components is related to the number of the surface sites of appropriate polarity. In the present paper the active carbon R4-ex (Norit) has been investigated after different chemical modifications of its surface (oxidation and thermal decomposition of the surface oxides).

1. EXPERIMENTAL

The mineral matter (ash) was removed from the commercially obtained active carbon R4-ex (Norit) by treatment with concentrated hydrofluoric and hydrochloric acids, so that its content in the carbon did not exceed 0.2%. Part of this carbon was used without any additional processing (sample N), the remaining part was chemically modified in two different ways. The oxidized sample (Ox) was prepared using concentrated HNO_3 at 353K. The reduced sample (HT) was obtained by heating at 1250K in an argon atmosphere.

In order to estimate the basis parameters characterizing the porous structure of the original and pretreated carbons, the benzene adsorption and desorption isotherms at 293K were determined by use of a McBain-Bakr sorption balance.

Next, the excess adsorption isotherms of benzene from binary mixtures in methanol, acetone and n-heptane were determined for these carbons at 293K using a immersion method [1]. For each composition, two flasks containing the same mixture were prepared. A known quantity of adsorbent (about 2g) was added to the weighed amount of mixture (about 4g) in one of the two flasks. The system consisting of the mixture and the adsorbent was agitated for 8 hr. The temperature was thermostatically controlled to 293±0.1K. After equilibration the supernatant solution was centrifuged and then analyzed by gas-liquid chromatography. The initial mixtures served for the detector calibration.

The specific surface excess of the preferentially adsorbed component 1 is expressed in the following form:

$$n_1^{\epsilon} = n^0(x_1^0 - x_1)/m \tag{1}$$

where n^0 is the total number of moles of the liquid mixture components being in contact with m grams of the adsorbent. x_1^0 and x_1 are the mole fractions of the first component in the initial and equilibrium mixtures, respectively.

2. RESULTS AND DISCUSSION

Figure 1 shows adsorption/desorption isotherms of benzene vapours for the investigated carbon samples.

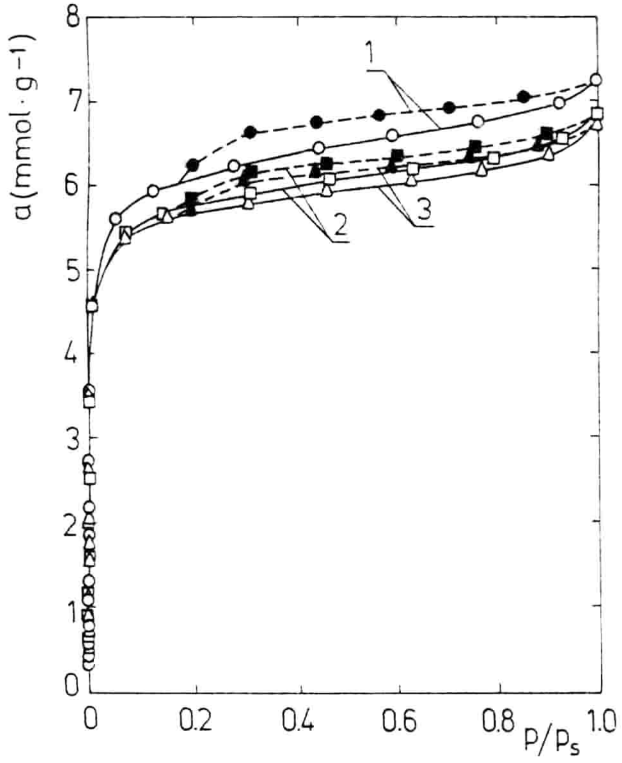

Figure 1. The adsorption (open points) and desorption (filled points) isotherms of benzene vapour on active carbons: 1 - N, 2 - HT, 3 - Ox at 293K.

On the basis of the adsorption data presented in Fig. 1 the surface areas of mesopores were calculated using Kisielev's method [5]. Moreover, the volumes of micropores V_{mi} and mesopores V_{me} were calculated according to Dubinin approach [6]. Appropriate numerical values of these parameters are collected in Table 1. As it is seen the oxidation process as well as heat treatment influence slightly the textural properties of the carbon samples.

Table 1
Parameters characterizing the porous structure of the active carbons investigated

Carbon	V_{mi} [cm^3/g]	V_{me} [cm^3/g]	S_{me} [m^2/g]
HT	0.476	0.131	62
N	0.495	0.148	71
Ox	0.471	0.121	57

For the three carbon samples the content of oxygen surface functional groups of an acidic character was determined by the method of neutralization of bases of various strenghts [7]. The content of the basic functional groups was determined by the method of neutralization of diluted HCl [8]. The concentrations of the surface functional groups for the investigated carbons are collected in Table 2. As expected the highest content of oxygen functional groups occurs in the case of sample Ox. Additionaly, the content of different surface species for carbons Ox, HT and N following their contact with methanol and acetone at the conditions similar to liquid adsorption experiment were determined (see Table 2). No significant changes in the number of the oxygen groups on the adsorbent surface after wetting with polar solvent are observed. Hence, one can assume that adsorption from the liquid phase is of exclusively physical character.

Table 2
Surface species on the surface of the active carbons

Carbon	Contenet of the surface functional groups (mmol·g^{-1})				
	-COOH	-COO-	OH	=CO	basic
HT	0.01	0.09	0.10	0.07	0.52
HT (methanol)	0.01	0.09	0.09	0.07	0.44
HT (acetone)	0.01	0.10	0.08	0.06	0.47
N	0.19	0.18	0.15	0.18	0.20
N (methanol)	0.19	0.18	0.11	0.17	0.20
N (acetone)	0.19	0.18	0.15	0.18	0.20
Ox	0.63	0.28	0.11	0.46	0.09
Ox (methanol)	0.60	0.26	0.35	0.54	0.10
Ox (acetone)	0.62	0.27	0.35	0.54	0.10

Figure 2 shows the excess adsorption isotherms of benzene, $n_1^e = f(x_1)$ from binary liquid mixtures for carbon samples HT, N and Ox, respectively.

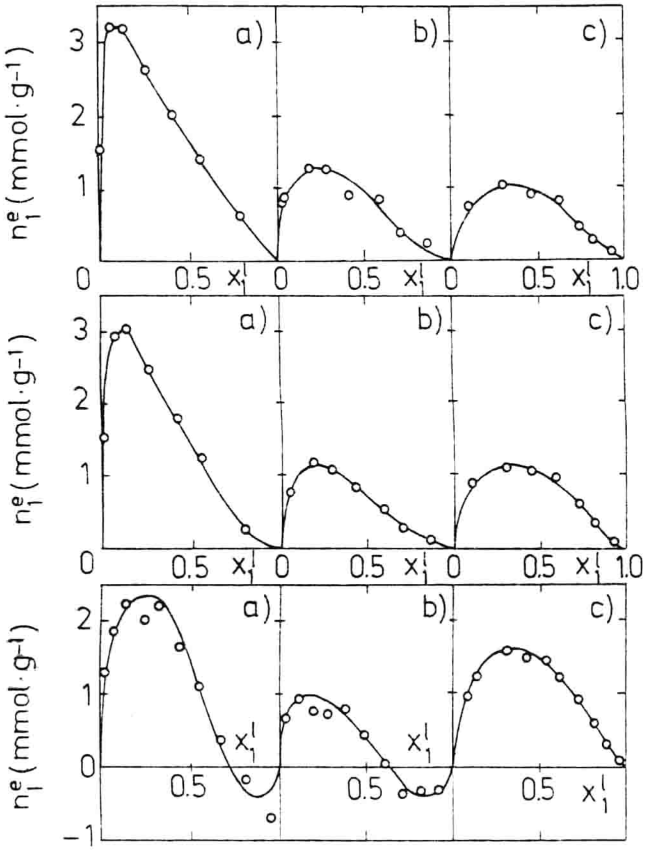

Figure 2. Specific surface excess isotherms of benzene from binary mixtures: (a) - benzene – methanol, (b) - benzene + acetone, (c) - benzene + n-heptane on carbon HT (top row), N (middle row) and Ox (bottom row) at 293K.

Comparing the adsorption isotherms in Figure 2, one can state that the chemical composition of the carbon surface strongly influences the extent of benzene adsorption from the liquid phase containing a second polar component. In the case of sample Ox, the excess adsorption isotherms of benzene from methanol and acetone mixtures show the presence of azeotropic point at which the composition of the bulk and surface phase are identical. For the benzene concentration in the bulk phase $x_1 > 0.7$ its excess adsorption becomes negative. It confirms the presence of the polar functional groups on the carbon Ox surface which interact preferentially with methanol and acetone molecules. The adsorption of benzene from n-heptane solution on carbon Ox is higher in comparison to carbons HT and N. Preferential adsorption of benzene in the whole concentration range for these samples may be explained by relatively strong interactions of aromatic ring with oxygen functional groups.

The surface layer capacities n^s for the investigated systems were determined using the isotherm equation describing the adsorption process from binary mixtures on energetically heterogeneous solid surfaces. The following linear form of this isotherm equation was taken into account [9]:

$$\left[-\ln\left(\frac{n_1^e}{n^s}+x_1\right)\right]^{1/2} = B^{1/2}\ln k - B^{1/2}\ln x \qquad (2)$$

where: $x = x_1/x_2$. B is a heterogeneity parameter determining the shape of the energy distribution function. k is a constant associated with the characteristic difference of the adsorption energies of both components of liquid mixture.

The parameters of eqn.(2) were obtained by fitting the straight line to the experimental points. The results of calculations (parameters n^s and k) are summarized in Table 3.

Table 3
Parameters of eq.(2) for the samples investigated

Mixture	Carbon	n^s [mmol·g^{-1}]	k
Benzene+ methanol	HT	1.1	58
	N	3.8	13
	Ox	3.8	3890
Benzene+ acetone	HT	2.0	46
	N	2.2	21
	Ox	2.6	2370
Benzene+ n-heptane	HT	2.3	22
	N	2.5	16
	Ox	3.5	12

Taking into account the n^s values from Table 3 the individual adsorption isotherms for binary liquid mixtures $n_i^s = f(x_i)$ were calculated. Real numbers of moles of i-th component in the surface phase, n_i^s were calculated according to the relation:

$$n_i^s = n_i^e + n^s \cdot x_i \qquad (3)$$

Figure 3 shows for illustrative purposes the individual adsorption isotherms for benzene + methanol and benzene + n-heptane mixtures on carbon samples Ox and HT.

The shape of these isotherms confirms dual character of the carbon Ox surface. In the case of benzene + methanol mixtures both components are present in the surface phase over the whole concentration range. In the case of benzene + n-heptane system above $x_1 \cong 0.5$ the surface phase contains practically benzene molecules only.

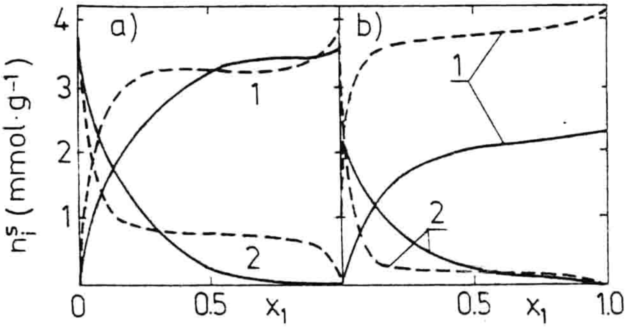

Figure 3. n_i^s as a function of x_1; (a) - carbon Ox, (b) - carbon HT. Broken lines - benzene (1) + methanol (2), solid lines - benzene (1) + n-heptane (2).

3. CONCLUSION

As a conclusion, one can say, that temperature and chemical treatment of active carbon changes its adsorption properties and consequently the selectivity of adsorption from the liquid phase. The investigation of adsorption of appropriate selected components give valuable information about the surface properties of carbon adsorbents.

4. ACKNOWLEDGEMENT

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5. REFERENCES

1 R.C. Bansal and T.L. Dhami, Carbon, 15 (1977) 153.
2 H. Jankowska, A. Świątkowski, J. Ościk and R. Kusak, Carbon, 21 (1983) 117.
3 A.M. Goncalves da Silva, V.A.M. Soares, J.C. Calado, M. Brotas de Carvalho, J. Chem. Soc. Faraday Trans., 87 (1991) 3799.
4 J. Goworek, J. Kaźmierczak and A. Świątkowski, Carbon 28 (1990) 849.
5 M.M. Dubinin in: Chemistry and Physics of Carbon (Ed. P.L. Walker,Jr.), Marcel Dekker, New York, 1966, vol.2, pp.51-120.
6 M.M. Dubinin, Carbon, 21 (1983) 359.
7 H.P. Boehm, E. Diehl, W. Heck and R. Sappok, Angew. Chem., 76 (1964) 742.
8 S. Weller and T.F. Young, J. Am. Chem. Soc., 70 (1948) 4155.
9 J. Ościk, A. Dąbrowski, M. Jaroniec and W. Rudziński, J. Colloid Interf. Sci., 56 (1976) 403.