Porosity Measurements of Cellulose Acetate Filters for Some Brands of Cigarette Using Mercury Porosimeter

Sameer H. Kareem and Inaam H. Ali
Chemistry Department / College of Science for Women / University of Baghdad

Received ٢7/8/2009 – Accepted 6/12/2009

الخلاصة

صممت الفلاتر لغرض تقليل كمية الدخان والمكونات الخاصة التي تدخل جسم المدخن، وان كفاءة هذه الفلاتر تتأثر بصفة خاصة بكل من المساحة السطحية والمسامية. لذلك كرس البحث الحالي لدراسة المسامية لخمسة انواع تجارية من السكائر ذات الفلاتر المصنوعة من خلات السيليلوز. وقد تم ذلك باستخدام جهاز دقيق لقياس المسامية الزئبقي، حيث قيس كل من قطر وحجم والمساحة السطحية للمسام وكذلك توزيع اقطار المسام.
واظهرت نتائج القياس ان حجم المسام ومساحتها السطحية لفلاتر الأنواع الخمسة من السكائر يمكن ترتيبها وفق التسلسل الآتي :-
Mercury > Sumer > Gauloises > Aspen > Pine
بينما اظهر منحني توزيع أقطار المسام قمة واحدة في اغلب النماذج المستخدمة ما عدا النماذج الخاصة بكل من سكائر (Pine) و (Aspen) ، حيث اظهرا قمتين وثلاث قمم على التوالي .

ABSTRACT

Filter is destined to reduce the quantity of smoke and specified components which fall in smoker’s body. The smoke removal efficiency is affected by the surface area and porosity of the filter fibers. Therefore, the present work is devoted to study the porosity of five brands of cigarettes with cellulose acetate filters. These are tested using an accurate instrument of Mercury intrusion porosimeter and the porosity parameters measured are pore diameter, pore volume, pore area, and pore size distribution.

The results showed that the pore volume and pore area of the five filters of cigarette can be arranged according to the following order:
Mercury > Sumer > Gauloises > Aspen > Pine
The pore size distribution obtained had only one maximum for all samples except for samples of Pine and Aspen which showed two and three maximum respectively.

Key words: Porosity, Cigarette Filter, Mercury Porosimeter, Pore area, Pore size Distribution

INTRODUCTION

In the early 1950's, the manufactures introduced the filtered cigarettes broadly following a spate of speculative announcements from doctors and researchers concerning a possible link between lung diseases and smoking, and by the 1960's, they dominated the market (1). Today, filtered cigarettes represented the majority of the market.

A filter has the purpose of reducing the amount of smoke, tar, nicotine, and fine particles inhaled during the combustion of a cigarette. In the “Light” cigarettes the filter is perforated with tiny holes in order to dilute the smoke air, as such, the inhaled smoke contains less tar and nicotine. It is reported (2) that the average smoke yields for tar and nicotine of U.S. cigarette for 1953-1996 decreased from 38 to 12 mg and from 2.7 to 0.85 mg respectively. Haag et al (3), reported that charcoal filter tips selectively remove certain volatile agents (such as hydrogen cyanide, formaldehydes, acrolein) from the smoke. Also, cellulose acetate filter tips remove from the smoke up to 75% of the carcinogeni, volatile N-nitrosamines (4), retain up to 80% of semivolatile phenols (5,6), and lower the yield of CO and nitrogen oxides (NOx) (7).

Y.S.Lee et al (8). Developed an activated carbon fibers with pore sizes and pore size distributions designed to efficiently adsorb specific toxins and to generate very little pressure drop in filter applications. The results showed that the porosity of fibers depended on the time of activation and the cross-sectional area of fibers, and had extremely high specific surface area (greater than 3000 m^2/g) and high degrees of meso-and macro-porosity. T. Sasaki et al (9) investigated the correlation between the adsorption efficiencies of the volatile organic compounds in cigarette smoke and pore size and pore volume of the activated carbons fibers. The results indicated that the adsorption efficiency relates to a weight of activated carbons. B.King and R.Borland (10) determined that both tar and nicotine yields correlated most strongly with filter density. Z. Chen et al (11) indicated that the removal efficiency of nicotine and tar by activated carbon was higher, which results from the fact that activated carbon has more suitable pore size and higher surface area for adsorption of nicotine and tar. P. Branton (12) used nitrogen adsorption at 77 K and mercury porosimetry to investigate the pores of activated carbon. The results indicated that increasing micropore volume leads to an increase in the removal efficiency of Ca. 40%, while the mesopores gave an improved removal efficiency of Ca. 20%.

Mercury intrusion porosimetry is used in previous work to test the porosity parameters in many areas, including filter material (13), nano fiber materials (14), Iraqi natural silica (15), certain Iraqi clays (16) , and pharmaceutical tablets (17).

In the present research, the porosity of some cigarette filters available in Baghdad market have been characterized. The measurements were performed using a fairly accurate and reliable instrument of mercury intrusion porosimeter.

MATERIALS AND METHODS

Five leading cigarettes varieties available for sale in Baghdad were identified. The packs of cigarettes were purchased in June 2009, and the specification of these variety were listed in table (1).

Table -1*: The specification of Cigarettes used in this research

Name	Company	Weight of tar/ mg	Weight of Nicotine /mg
Sumer	Iraqi Company of Tobacco and Cigarette	12	0.8
Pine	KT and G/ Korea	5	0.4
Aspen	JTI Macdonald Corp/ Germany	12	0.8
Gauloises	SEITA FRANCE/ European Union	4	0.4
Mercury	I.T.C (H.K.J) Mercury Cigarette and Trading Corp. L.T.D. U.S.A	12	0.8

* Specification was get from cigarbox

Smoke yields of cigarettes are also dependent on physical parameters, such as, length of cigarette and filter and circumference of the cigarette and filter (18). The cigarettes used in this work have the following construction properties listed in table (2).

Table -2: The construction properties of filtered cigarettes used.

Name	Cigarette Length/ cm	Cigarette Diameter/ cm	Filter Length/cm	Filter * Weight/ g	Filter Density (g/cm^3)
Sumer	8.45	0.80	2.00	0.1267	0.1261
Pine	8.30	0.80	2.35	0.1336	0.1132
Aspen	8.30	0.75	2.10	0.1135	0.1224
Gauloises	8.30	0.80	2.70	0.1371	0.1011
Mercury	8.30	0.75	2.00	0.1026	0.1162

* Five cigarette filters weighted in analytical balance.

The measurements of porosity parameters were made using mercury porosimeter, model "poresize 9320', obtained from micromeritics, USA. This instrument characterize the pores ranging from 0.006 mm to 360 mm and capable of generating pressures ranging from 0 to 30.000 psi. The mercury porosimeter is a device which is capable of measuring simultaneously both the pressure and the volume of the mercury taken up by the pores. The measurements was carried out as follows (15-17):-

The coating of filter was separated from the remaining filter material, and only pure filter material was used for analysis. The filter specimen to be examined was weighted using an analytical balance and dried in vacuum oven at (120 °C) overnight. After drying process, the specimen was transferred to the low pressure champer and the measurements proceeded automatically recording the pressure (in Psi) and intrusion reading (in PF) (PF= pico farad). The same procedure were employed after the sample was transferred to the high pressure chamber. The duration time of the experiment lasted about 5 hours.

RESULTS AND DISCUSSION

The filter density was calculated from observed filter weight, length, and diameter. The results obtained (Table 2) indicate that the filter density of various brands cigarette follow the sequence:

Sumer > Aspen > Mercury > Pine >Gauloises

The filter of high density slowing the flow of smoke through the filter. This results in a higher retention of particulate matter by filter tip (19). Moreover, the smoke velocity is seen to decrease with increased in the diameter.

The porosity or pore system of a porous sorbent material can be characterized in many different ways. The most important physical methods are (20-22): Mercury intrusion porosimetry, Helium measurements, and Gas adsorption (N_2, Ar, CO_2). Mercury porosimeter experiments often gives valuable information concerning the macro- and meso-pores of sorbent and hence very well may be used for quality tests of sorbent samples. In the measurement; the porous material is immersed in a non-wetting liquid will cause it to penetrate into the pores of the solid until equilibrium against the surface tension (γ) in the smaller and smaller pores is attained. The respective mechanical equilibrium condition leads to the so-called Washburn equation for the limiting pore diameter (D) into which mercury at pressure (P) can penetrate : $D = - 4 \cos \Theta / P$

Where Θ is the contact angle between the mercury meniscus and the pore wall. The practical value of this parameter is 140°,while the value of (γ) for mercury is 480 dynes/cm. Pressures and intrusion volume were measured with better than 0.25% accuracy. Typical data obtained on filter of sumer cigarette were tabulated in table (3), which are show a pore size distribution data form and pore area distribution data form.

Table -3 :- Pore volume and pore area distribution data for Sumer cigarette filter

Pressure Psia	Pore size um	Intrusion Reading	Cumulative Intrusion	Cumulative Pore volume cc/g	Average Pressure Psai	Incremental Pore volume cc/g	Average Pore size µm	Incremental Pore area m^2/g	Cumulative Pore area m^2/g
1.2	150.650	65.65	....	....	....	....	....	....	....
2.8	64.564	65.24	0.05	0.00427	2.00	....	90.39	....	0.00019
4.7	38.464	64.19	1.10	0.09405	3.75	0.08978	48.208	0.00745	0.00780
6.4	28.247	59.79	5.50	0.47025	5.55	0.3762	32.573	0.04619	0.05774
8.6	21.021	55.51	9.78	0.83619	7.50	0.36594	24.104	0.0607	0.13876
9.4	19.232	50.88	14.41	1.23205	9.00	0.39586	20.087	0.0788	0.24535
10.1	17.899	49.89	15.40	1.31670	9.75	0.08465	18.542	0.0183	0.28405
11.3	15.998	49.80	15.49	1.32440	10.70	0.0077	16.895	0.00182	0.31355
12.0	15.065	49.77	15.52	1.32696	11.65	0.00256	15.518	0.00067	0.34205
12.6	14.348	49.77	15.59	1.33294	12.30	0.00598	14.698	0.00163	0.36276
13.2	13.695	49.65	15.64	1.33722	12.9	0.00428	14.014	0.00122	0.38168
13.5	13.391	49.64	15.65	1.33807	13.35	0.00085	13.542	0.00025	0.39525
61	2.964	41.87	23.42	2.00241	....	....	....	....	......
1079	0.1675	40.06	25.23	2.15716	570	0.15400	0.3172	1.9423	27.207
3104	0.0582	40.02	25.27	2.16058	2091.5	0.003415	0.0864	0.1581	54.6823
5332	0.0339	39.91	25.38	2.16999	4218	0.009410	0.0429	0.8782	202.519
7733	0.02337	39.80	25.49	2.17939	6532.5	0.00940	0.0277	1.3588	315.054
9319	0.01939	39.77	25.52	2.18196	8526	0.00257	0.0120	0.4848	411.632
10394	0.01739	39.73	25.56	2.18538	9856.5	0.00342	0.0183	0.7459	476.637
11640	0.01553	39.69	25.60	2.18880	11017	0.00342	0.0164	0.8337	533.560
12515	0.01444	39.68	25.61	2.18960	12077.5	0.00080	0.0149	0.2179	585.142
13144	0.01375	39.49	25.80	2.20590	12829.5	0.01630	0.0114	4.6274	626.232
14129	0.01279	39.38	25.91	2.21530	13636.5	0.00940	0.0133	2.8362	668.418
14822	0.01219	39.36	25.93	2.21700	14475.5	0.001695	0.1249	0.5429	710.122
14777	0.01223	39.33	25.96	2.21958	14799.5	0.00258	0.1222	0.8449	726.837

Converting intrusion meter readings to pore volumes requires, first, calculating cumulative changes in capacitance (initial value taken as zero). These changes in capacitance are then multiplied by the conversion factor (penetometer constant) supplied for the penetometer and a units conversion factor to give the cumulative pore volume. Cumulative pore volumes per gram of sample are obtained by dividing by the weight of the sample.

The total pore surface area obtained by assuming that all the pores are cylindrical capillaries. Then the pore surface are (A) for each diameter increment is simply related to incremental pore volume (v) and the average pore diameter (D) by equation:

$$A = 4V/ D$$

The cumulative surface area for each point is the sum of these for all preceding points.

The results obtained on the five filters are summarized in Table (4), in which the experimental values of pore volume, pore area, the most abundant pore diameter, and median pore diameter of the five different filtered cigarettes have been tabulated. The value of D on the distribution curves corresponding to the maximum value of $\Delta V/ \Delta D$ is called the most abundant pore diameter, while median pore diameter is the pore diameter at which 50% of the total intruded volume of mercury is intruded into the sample.

Table -4: The porosity parameters of the different filters

Sample	Pore volume cc/g	Pore area m^2 /g	Median pore diameter / µm	Most abundant pore diameter / µm
Sumer	2.21958	726.837	20.087	0.014
Pine	0.03433	10.998	0.019	0.013
Aspen	1.59137	485.684	40.200	0.016
Gauloises	2.14132	685.222	30.130	0.013
Mercury	3.45382	1103.460	22.500	0.013

The results of table (4) show that the pore volume and pore area of the five filters of cigarette in an order that may be arranged in sequence:

Mercury > Sumer > Gauloises > Aspen > Pine

This suggest that filter of Mercury can be reduced the quantity of tar and nicotine in the inhaled smoke larger than the others, and the sequence can be arranged as above.

The pore size distribution as determined were 0.012**µ**m to 226 **µ**m, 0.012 **µ**m to 150 **µ**m, 0.012 **µ**m to 150 **µ**m, 0.013 **µ**m to 226 **µ**m, and 0.012 **µ**m to 2.9 **µ**m for the filters of Mercury, Sumer, Gauloises, Aspen, and Pine cigarettes respectively.

Using IUPAC definitions of pore size (23), we have a mesopore volume of 0.059, 0.051, 0.049, 0.039, and 0.027 cc/ g for filters of Sumer, Mercury, Gauloises, Aspen, and Pine cigarettes respectively, while the macropore volume were 3.403, 2.161, 2.092, 1.552, and 0.007 cc/ g for Mercury, Sumer, Gauloises, Aspen, and Pine cigarettes respectively. The results show that most of the pore volume is assigned to macropores except on the sample of Pine. In contrary, the results show that the pore area is assigned to mesopores. The narrow range of pore size distribution is indicated on filter of Pine cigarette , while the wider range is indicating on filters of Mercury and Aspen, suggesting that the adsorption properties of the filter of Mercury and Aspen has higher adsorption efficiency for volatile organic compounds than the filter of Pine.

The mercury porosimeter measurements yield a cumulative pore volume starting at the widest pores. From these data a pore size distribution can be derived by plotting the increase in pore volume with each smaller pore diameter ($\Delta V/ \Delta D$) that becomes accessible. The pore size distribution obtained (figs.1 – 5) had only one maximum for all samples except for samples of Pine and Aspine which showed two and three maximum respectively. Also, the maximum of pore size distribution were shifted to smaller values on samples of Mercury, Sumer, and Gauloises cigarettes. In addition, although the pore size distribution had about a similar shape, the intensities of the curves were different.

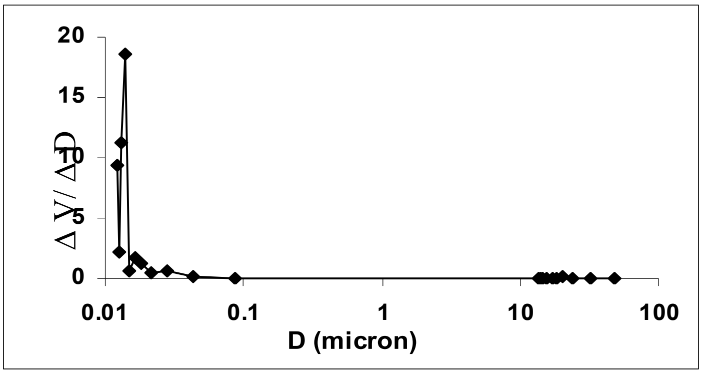

Fig -1: Pore volume distribution over pore diameter for Sumer Cigarette filter

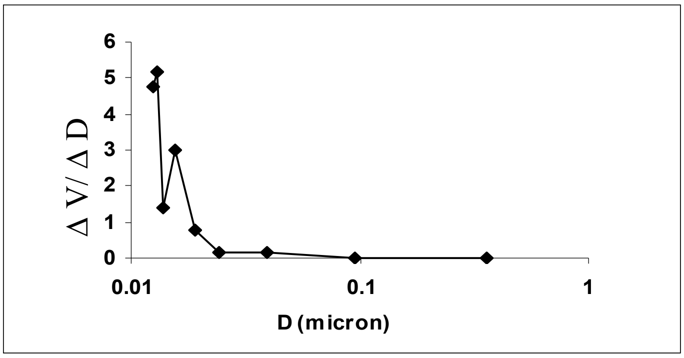

Fig -2: Pore volume distribution over pore diameter for Pine Cigarette filter

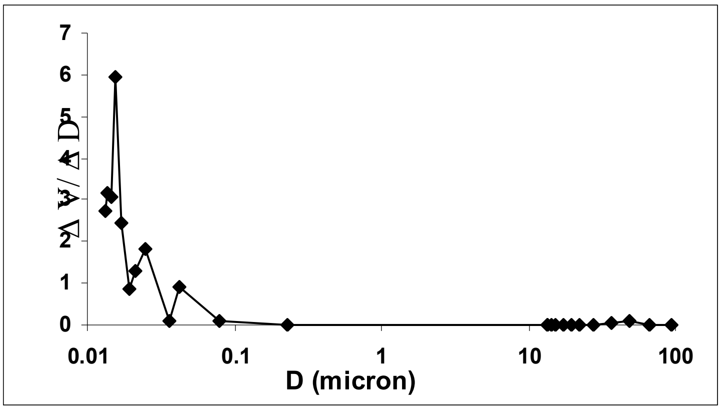

Fig -3: Pore volume distribution over pore diameter for Aspen Cigarette filter

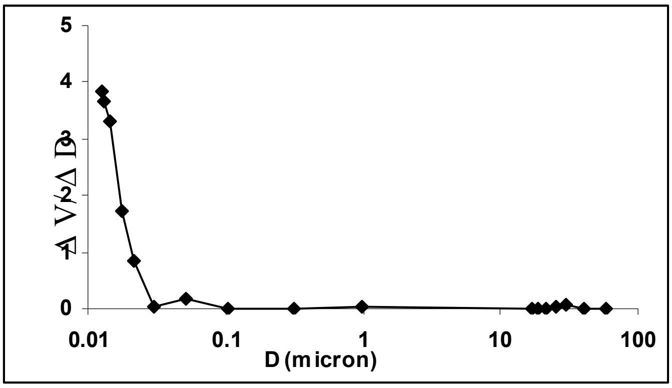

Fig -4: Pore volume distribution over pore diameter for Gauloises Cigarette filter

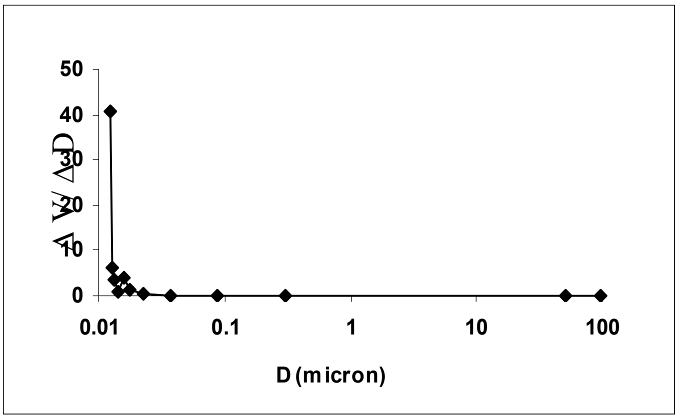

Fig -5:Pore volume distribution over pore diameter for Mercury Cigarette filter

In conclusion, we can summarize the followings:-

1- The filter density of various brands cigarette follows the sequence:

Sumer > Aspen > Mercury > Pine >: Gauloises

2 - The pore volume and pore area of the five filters of cigarette in an order that may be arranged in sequence:

Mercury > Sumer > Gauloises > Aspen > Pine

3 - Most of the pore volume is assigned to macropores except on the sample of Pine, while most of the pore area is assigned to mesopores.

4 - The pore size distribution obtained showed only one maximum for all samples except for samples of Pine and Aspine which showed two and three maximum respectively.

REFRENCES

1- K.J. Norton, K.Wilkins, and R. O'Connor "New Zealand Tobacco product Testing' Research Laborotary report, Roswell Park Cancer Institute, p.3 (2008).

2- D. Hoffmann, I. Hoffman, and E.L. Wynder. "The changing cigarette, 1950-1997. Facts and expectations". In report of Canada's Expert commite on cigarette Toxicity Reduction (Rickert W.S., Ed.) Chapter 11 p. 94, Health Canada, Ottawa, Canada(1998) .

3- H.B. Haag, P.S. Larson, and J.H. Finnegan " Effect of filtration on chemical and irritating properties of cigarette smoke" AMA Arch. Otolaryngol, 69, 261-265. (1969).

4- K.D.Brunnemann, L.Yu, and D. Hoffmann "Chemical studies on tobacco smoke XV11. Assessment of carcinogenic volatile N-nitrosamines in tobacco and in mainstream and side stream smoke from cigarettes" Cancer Res., 37, 3218-3222, (1997).

5- D. Hoffman, and E.L. Wynder " Filtration of phenols from cigarette smoke, J. Natl. Cancer Inst. 30, 67-84, (1963).

6- A. W. spears " Selective Filtration of volatile phenolic compounds from Cigarette smoke. Tob. Sci. 7, 76-80, (1963).
7- National Cancer Institute," Smoking and Health Program Toward Less Hazardous Cigarettes", DHEW Publ. No. (NIH) 77 – 128,(1977) .
8- Y.S. Lee, Y.V. Basova, D.D. Edie, L.K. Reid, S.R. Newcombe, and S.K. Ryu, "Preparation and characterization of trilobal activated carbon fibers" Carbon 41, 2573-2584 (2003).
9- T. Sasaki, A. Matsumoto, and Y.Yamashita "The effect of the pore size and volume of activated adsorption efficiency of vapor phase compounds in cigarette smoke" Colloids and Surfaces A: Physicochemical and Engineering Aspects 325 (3), 166-172, (2008).
10- B. king, and R. Borland "The low tar-strategy and the changing construction of Australian Cigarettes" Nicotine and tobacco research, 6(1), 85-94, (2004).
11- Z. Chen, L. Zhang, Y. Tang, and Z. Jia, Adsorption of nicotine and tar from the mainstream smoke of cigarettes by oxidized carbon nanotubes" Applied surface science, 252, 2933-2937, (2006).
12- P. Branton, An. H. Lu, and F. Schüth, "The effect of carbon pore structure on the adsorption of cigarette smoke vapour phase compounds", Carbon, 47, 1005-1011, (2009).
13- Jena, A. and Gupta K. "Charactrization of pore structure of filtration media containing hydrophobic and hydrophilic pores" Fluid/ particle separation Journal. 14, 1-6, (2002).
14- Jena, A and Gupta, K. " Pore volume Nanofiber Nonwovens, " International Nonwovens Journal, Summer, 24-30, (2005).
15- Kareem, S.H. "Porosity of certain Iraqi natural Silica by mercury porosimetry measurements" Journal of Al-Nahrain, 10 (1), 1-6, June (2007).
16- Saher. S.H., " Investigation of the porosity of certain Iraqi clay deposites by mercury porosimeter" Um- Salama Science Journal, 6 (1) 2009.
17- S. K. Ibrahim, " Study of the porosity of certain pharmaceutical tablets using intrusion Mercury porosimeter" Um-Salama Science Journal. (2009) *(in Press)*.
18- D. Hoffmann, I. Hoffmann, and K. El-Bayoumy "The less Harmful cigarette: A controversial Issue. A Tribute to Ernst L. Wynder" Chem. Res. Toxicol. 14 (7), 768-790, (2001)
19- D.Hoffmann, I.Hoffmann," The Changing Cigarette 1950 – 1995 " , Journal of Toxicology and Enviromental Health, 50 , 307 – 364, (1997) .
20- D.K. Chakrarty and B. Viswanathan, " Heterogenous Catalysis" New Age Internationa (P) Ltd., Publishers, 1st edition, p. 63(2008).

21- P. Klobes, K. Meyer and R. G. Munro, “Porosity and specific surface area measurements for solids Materials” Special Publications, U.S. government Printing Office, p. 40(2006).
22- J. Keller, and R. Staudt, “Gas Adsorption Equilibria : Experimental methods and Adsorption isotherms”, Springer Science and Business Mediia, Inc. Boston, p32(2005).
23- K.S.W. Sing, DH Everet, R. Haul, L. Moscou, R. Pierothi, and J. Rouquero, “ Physisorption data for gas/ solid systems”, Pure Appl. Chem, 57 (4), 603,(1985).