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GASIFICATION REACTIVITY OF CANADIAN ANTHRACITE
AND SEMI-ANTHRACITE CHARS

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ABSTRACT

This paper presents the gasification reactivity in air of both the untreated and demineralized chars derived from Canmore (semi-anthracite) and Mt. Klappan (anthracite) coals using a thermogravimetric analysis technique. The effects of mineral content, particle size, and surface area on the reactivity of these chars were investigated. It was found that the gasification reactivity of the char decreased with increased particle size and decreased mineral content. The surface sub-fractal dimension, \bar{D} , was determined from logarithmic plots of gasification reactivity against particle size. This parameter is a measure of the surface irregularity as experienced by species reacting at or with a surface and $2 < \bar{D} < 3$. The values determined for \bar{D} were 2.78 and 2.40 for Canmore and Mt. Klappan chars respectively. The specific surface area measured by carbon dioxide adsorption at 298 K did not correlate with reactivity or particle size data whereas the results from mercury porosimetry indicated possible correlations.

INTRODUCTION

Coal gasification as an option for the production of gaseous and liquid fuels has been a subject of interest in Canada. Recent studies at the Energy Research Laboratories have indicated that the chemical and physical properties of Canadian coals are quite

similar to American coals in many respects¹⁻³. Generally, the gasification reactivity of a coal increases with a decrease in rank and with increased N₂ apparent surface area. Similarly, the reactivity of char increases with decrease of rank of the parent coal. Inherent minerals in the parent coal, such as calcium oxide and magnesium oxide, serve to increase the char reactivity³⁻⁵. It has been suggested that the particle size of the char also has some effects on reactivity but this phenomenon has not been quantified⁶.

Coals and their chars are complex heterogeneous materials and a complete description of all of the chemical and physical mechanisms that control gasification is not yet available. As part of a continuing research program the objectives of the present study were to examine the effects of mineral matter, particle size and surface physical properties on the gasification in air of two Canadian high rank coals. The coals were selected for this study because of their high carbon and low volatile matter contents to minimize the effects of heteroatomic species. In addition, one of the coals was selected because of its high ash content in order to assess the catalytic effects of mineral matter. There may be a potential world market for such high rank coals in the near future.

EXPERIMENTAL

The chars used in the present study were derived from Western Canadian coals - Canmore (semi-anthracite) and Mt. Klappan (anthracite). These particular samples were selected primarily because of their low gasification reactivity. Coal demineralization was accomplished using a method described by Morgan et al⁷ and Bishop and Ward⁸. A 300 g sample of coal was stirred at 328 K in 350 mL of 5N HCl for 1 h. The acid was decanted and an equal volume of 24N HF was added with the temperature maintained in the range of 328 to 333 K. After 1 h with occasional stirring, the coal was filtered and rinsed with distilled water. The demineralized coal was then washed with 12N HCl, refluxed with distilled water for 2 h, and air dried. According to Bishop and Ward⁸, treatment of coal by

this method causes no alteration of carbon or hydrogen content. The effects of demineralization by this method on anthracite chars is not well understood.

Each coal sample (180 g, particle size 3 to 6 mm) was heated in a muffle furnace in flowing N_2 ($3L\ min^{-1}$) from 293 to 1273 K at a rate of $10\ K\ min^{-1}$ and further charred at 1273 K for 30 min as in previous studies³. The sample was then cooled in N_2 and ground. The char samples were divided into four particle size ranges by sieving:

Fraction	Size range (μm)	Sieve number (U.S. standard)
A	297 - 250	50 - 60
B	200 - 177	70 - 80
C	149 - 125	100 - 120
D	105 - 89	140 - 170

The size range was chosen based on an earlier study on the effects of coke particle size on gas adsorption measurements as described by fractal geometry⁹. Gasification reactivity was determined at 773 K in dry air ($500\ mL\ min^{-1}$) using a Cahn electrobalance as described previously². Apparent surface areas were determined in a conventional volumetric apparatus using CO_2 at 293 K. The Dubinin-Radushkevich-Kaganer¹⁰ (DRK) equation was used to derive the apparent surface area by using 3.69 MPa as the saturation vapour pressure and $0.17\ nm^2$ for the effective cross-sectional area of CO_2 . Mercury porosimetry was carried out on a Micromeretics porosimeter, and proximate analysis was performed using a Fisher 490 analyzer. Carbon, hydrogen and nitrogen contents were determined using a Perkin-Elmer 240 CHN analyzer and sulphur was determined using a Leco analyzer. Particle size analysis of selected samples was obtained by R. Trottier, Fineparticle Research Institute, Laurentian University, Sudbury, Ontario.

RESULTS AND DISCUSSION

Proximate and ultimate analyses of the coals and chars are presented in Table 1. Clearly, the charring process removed approximately 85% of volatiles and the ultimate analyses indicated an increase in carbon content at the expense of hydrogen in all cases. The Mt. Klappan coal contains a considerable amount of ash which is effectively removed by the demineralization method to produce a char of approximately the same ash content as the Canmore char. Examination of Table 1 indicates that the two demineralized chars used in this study were of similar chemical composition.

Chemical analyses of the ash from the coal and char samples are summarized in Table 2. Again, the similarity of the ash in the demineralized chars is obvious. The charring process alone, however, removes some aluminum from the ash of Mt. Klappan coal. The Mt. Klappan coal and char contain significantly more iron and nickel species than Canmore. The mineral matter is effectively removed by demineralization. The results presented in Tables 1 and 2 suggest that an activity comparison of the two demineralized chars would be appropriate since the effects of the mineral content should be approximately equal. The effects of mineral content on gasification reactivity should also be apparent from the results comparing the original and demineralized chars.

Typical TGA results for char gasification are presented in Figure 1. The weight loss curve may be separated into two regions of approximately constant rate of weight-loss. A shrinking core model has been proposed to explain this phenomenon⁴. Reaction was thought to occur on the outside surface of the individual particles and proceed inwards, leaving behind a layer of ash. The rate-controlling step was thought to change from the initial kinetically-controlled region to a diffusion-controlled region where heat and mass transfer determine chemical reactivity. A previous thermogravimetric study of the rate of weight increase corresponding to oxygen adsorption on coke at 473 K indicated a similar two-stage reaction where the reaction rate measured in the second region was related to the

fractal geometry inherent in that particular system¹¹.

In the present study, the char gasification reactivity was determined from the slope of the initial region of the weight loss versus time curve as in equation 1:

$$r_{\max} = W_0^{-1} (dW/dt) \quad (1)$$

where r_{\max} is the maximum reactivity ($g\ g^{-1}\ h^{-1}$), W_0 is the initial mass of the char on a dry, ash-free basis, and (dW/dt) represents the maximum rate of weight loss as determined graphically from Figure 1. The maximum rate does not necessarily occur at time zero, so that this is not an initial rate.

The results of the gasification reactivity study are summarized in Table 3 along with the average particle diameter calculated from the minimum and maximum sieve sizes, the apparent surface area and the total pore volume. Recent work has indicated that data from gas adsorption^{9,11} and mercury porosimetry¹² could be analyzed using fractal geometry. It has been demonstrated that surface fractal dimension, D_s , is a working parameter to describe surface roughness¹³ and further that analysis of the chemical reactivity of surfaces yields a surface sub-fractal dimension, \bar{D} ^{13,14}. The surface sub-fractal dimension as experienced by reactants at a surface may be lower than the fractal dimension, D . For many surface reactions, it has been shown that the rate of reaction, r , is related to the sub-fractal dimension by the expression:

$$r \propto \text{reactive surface area} \propto R^{\bar{D}-3} \quad (2)$$

where R is particle radius and the \bar{D} value refers to the surface irregularity as experienced by the reactants.

The reactivity data were therefore plotted in log-log fashion against particle radius (Figure 2). The self-similarity of these chars with regards to gasification of various par-

ticle sizes is therefore established by the linear plots obtained for all chars. In general, the gasification reactivity increased with decreased char particle size for both untreated and demineralized samples. This effect agrees with the data reported by Tseng and Edgar¹⁵ in their study of a char derived from an American anthracite coal. The sub-fractal dimensions calculated from equation 2 for the chars are summarized below:

Char sample	Sub-fractal dimension, \bar{D}
Canmore	2.78 \pm 0.08
Demineralized Canmore	2.36 \pm 0.28
Mt. Klappan	2.40 \pm 0.18
Demineralized Mt. Klappan	2.62 \pm 0.12

The deviations given above correspond to the error interval for 95% confidence. Fractal analysis of the apparent surface area (pore volume) and particle size data did not yield reasonable relationships. As shown in Figure 3, plots of mercury intrusion volume against particle diameter indicate that intrusion volume increases with decreased particle size. Obviously, such geometric resolution analysis depends upon the value used for equivalent particle diameter and this in turn depends upon the underlying assumption of spherical particles. Since Figures 2 and 3 use an average particle diameter as determined from the minimum and maximum sieve sizes, it was necessary to measure the particle size distribution by an alternative method. In Figure 4, the mean value for maximum particle diameter as determined by image analysis is plotted against the average particle diameter for Canmore char and demineralized Canmore char. The resulting linear relation indicates that the assumptions involved in calculating an equivalent particle diameter are reasonable.

Examination of Table 3 can lead to some qualitative results. There is no systematic variation of apparent surface area with particle size. There have been suggestions in the

literature that surface area determinations using CO_2 at 298 K be considered as 'absolute' values since this was the highest value measured for some carbon surfaces¹⁶. An ideal fractal surface, on the other hand, has a specific surface area which increases to infinity with decreased particle size or decreasing adsorbate size. A recent review of coal structure indicated that coals may well be described by fractal geometry¹⁷ and work in our laboratory^{9,12} has indicated that apparent surface areas for coals, chars and cokes are dependent on particle size and sample history in addition to the methods used to determine the values. The data generated by mercury porosimetry (Figure 3) are interesting for several reasons. There is an increase in intrusion volume with decreased particle size. The fact that a volume fractal dimension has not yet been calculated from these data is aggravated by the difficulty in separating inter- and intraparticle volume. There is also little difference between the total pore volume of chars and demineralized chars of similar size range.

Some general comments regarding fractal dimension, apparent surface area and pore volume can be made. It has been demonstrated that the process of activating a charcoal resulted in a lowering of surface fractal dimension from 3.00 to 2.00 with concomitant increase in apparent surface area as determined by N_2 or a series of hydrocarbons^{18,19}. Similarly, the process of demineralization by strong acid treatment is expected to smooth the original pores of the coal and change the resulting char from predominantly microporous to mesoporous. This implies a change from high \bar{D} (2.78) to lower \bar{D} (2.36) value as exhibited by the Canmore char. In addition, a more microporous char is expected to have a higher apparent surface area as is the case for Canmore char. If demineralization simply smoothens the pores, then one would expect the apparent surface area to decrease and again this occurs for Canmore char. If the process of pore smoothing included pore widening so as to open up more void space, one would expect demineralization to produce an increase in apparent surface area and mercury intrusion volume but such is not the case for these chars. The activity of the untreated Mt. Klappan char appears exces-

sively high particularly since the derived surface sub-fractal dimension is low. This char, however, contains substantial mineral matter including 0.6 wt % of CaO (Table 2) which may have a catalytic effect on the rate of gasification^{3,6}.

Table 3 clearly shows that the Mt. Klappan char exhibits relatively high reactivity values and a relatively low value of surface sub-fractal dimension. This higher reactivity must be due to the mineral matter. In discussing gasification reactivity one must consider the 'absolute' value for each particle size (and sample history) as well as the rate of change of this value with particle size. The removal of significant quantities of ash from Mt. Klappan coal followed by charring did not significantly alter the apparent surface area or pore volume compared to untreated Mt. Klappan char. On an ash-free basis, however, this char would exhibit values similar to as those for Canmore char. Therefore, the ash increases the char reactivity but at the same time, the reactivity does not change as rapidly with decreased particle size as does the demineralized char. The data in Figure 2, for example, indicate that for larger particles (>250 μm radius) examined at the present conditions, Canmore char reactivity would appear higher than Mt. Klappan char. Earlier work by Hippo and Walker²⁰ indicated that char reactivity for CO_2 gasification exhibited an increase in reactivity with decreased particle size. A study by Radovic, Walker and Jenkins²¹ on char gasification in air indicated that reactivity was independent of particle size over a similar particle size range. Surface accessibility is often cited as a rate-determining step in thermal analysis studies. The concept of a shrinking core model based upon a particle of Euclidean shape or geometry should be extended to consider particles of irregular shape where the accessible surface may well be described by fractal geometry.

In summary, since there is an obvious increase in anthracite and semi-anthracite char gasification reactivity with decreased particle size as quantified by a fractal dimension, the overall gasification rates of these chars depend primarily on geometric factors under the conditions specified. There was no obvious correlation between reactivity and apparent surface area (DRK, CO_2 , 298 K). Reactivity increased with increased total

mercury intrusion volume and correspondingly, intrusion volume increased with decreased particle size. For any char particle size, gasification reactivity appeared to increase with surface sub-fractal dimension in the absence of mineral matter effects. Demineralized chars exhibited lower gasification reactivity than untreated chars. The reactivity of a char will be affected by surface structure and pore geometry (surface accessibility) or mineral content.

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Table 1 Coal and char analysis

Sample	Proximate analysis, wt %			Ultimate analysis, wt %			
	Ash	Volatile matter	Fixed carbon	C	H	S	N
Canmore							
coal	11.6	12.2	76.2	80.5	3.4	0.8	1.6
char	11.2	2.1	86.7	86.4	0.4	0.8	1.4
Demineralized							
Canmore							
coal	3.8	11.6	84.6	87.8	3.7	0.8	1.6
char	6.6	1.2	92.2	91.1	0.4	0.8	1.3
Mt. Klappan							
coal	52.1	9.0	38.9	42.2	1.4	0.3	0.6
char	39.3	1.4	59.3	61.3	0.3	0.4	0.7
Demineralized							
Mt. Klappan							
coal	5.4	8.1	86.5	87.4	2.4	0.5	1.1
char	5.3	1.3	93.4	94.0	0.3	0.5	1.1

Table 2 Ash analysis, wt %

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	NiO
Carmore									
coal	7.0	3.3	0.3	0.2	0.1	0.1	0.0	0.2	0.0
char	6.8	3.2	0.3	0.2	0.1	0.1	0.0	0.2	0.1
Demineralized Carmore									
coal	2.3	1.2	0.0	0.1	0.0	0.0	0.0	0.0	0.0
char	4.0	1.9	0.2	0.1	0.0	0.0	0.0	0.1	0.1
Mt. Klappan									
coal	27.5	12.5	4.8	0.5	0.7	0.3	0.2	0.7	2.6
char	24.0	6.7	4.6	0.4	0.6	0.8	0.5	0.6	0.0
Demineralized Mt. Klappan									
coal	3.2	1.6	0.1	0.1	0.1	0.0	0.0	0.0	0.0
char	3.7	0.9	0.1	0.2	0.1	0.0	0.1	0.0	0.0

Table 3 Particle size effects

Char	Particle diameter (μm)	Reactivity (g/g-h)	Surface area (m^2/g)	Pore volume (mL/g)
Carmore	270	0.75	135	0.42
	200	0.81	112	0.53
	140	0.83	113	0.69
	100	0.95	124	0.71
Demineralized Carmore	270	0.36	78	0.19
	200	0.45	68	0.57
	140	0.48	79	0.63
	100	0.72	85	0.78
Mt. Klappan	270	0.85	62	0.16
	200	1.01	56	0.50
	140	1.38	84	0.65
	100	1.50	89	0.74
Demineralized Mt. Klappan	270	0.47	74	0.27
	200	0.53	84	0.68
	140	0.64	74	0.73
	100	0.67	66	0.76

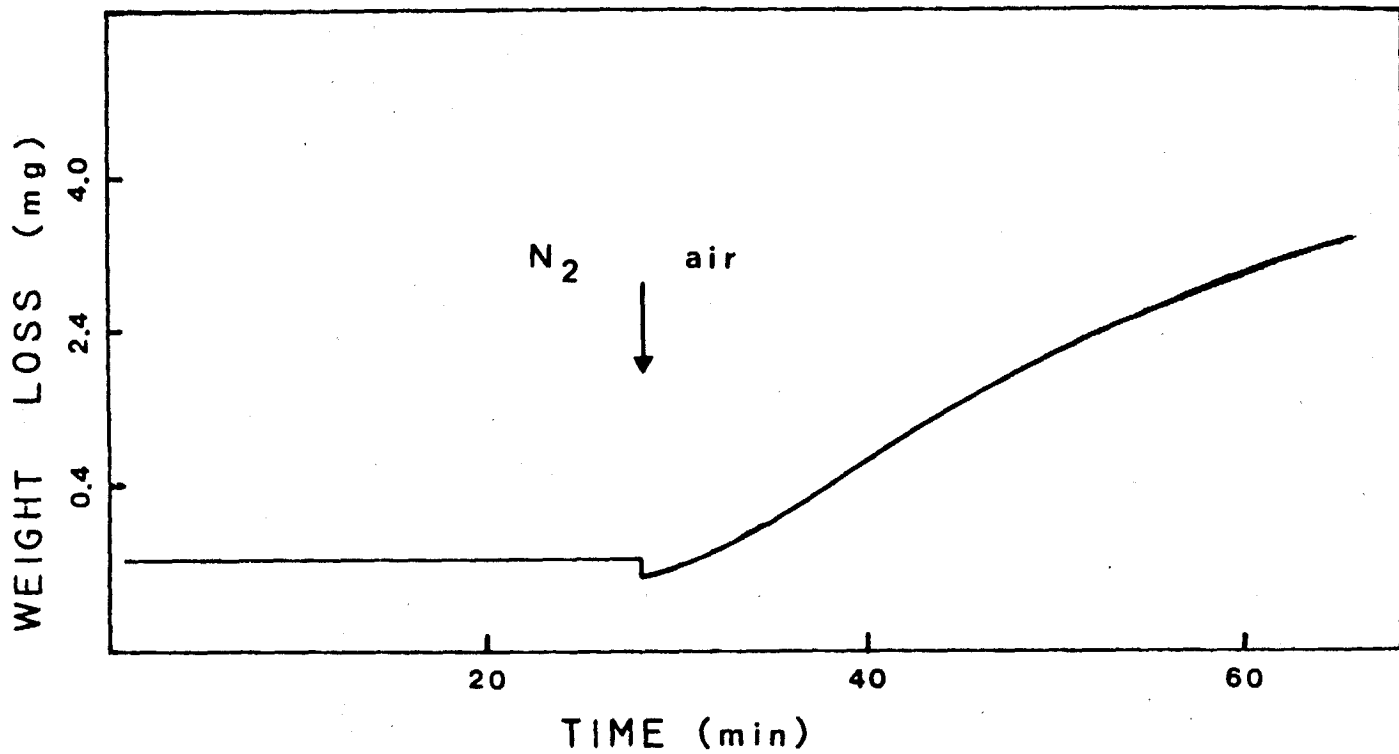


Figure 1. Thermogravimetric analysis of untreated Canmore char 100 μm diameter.

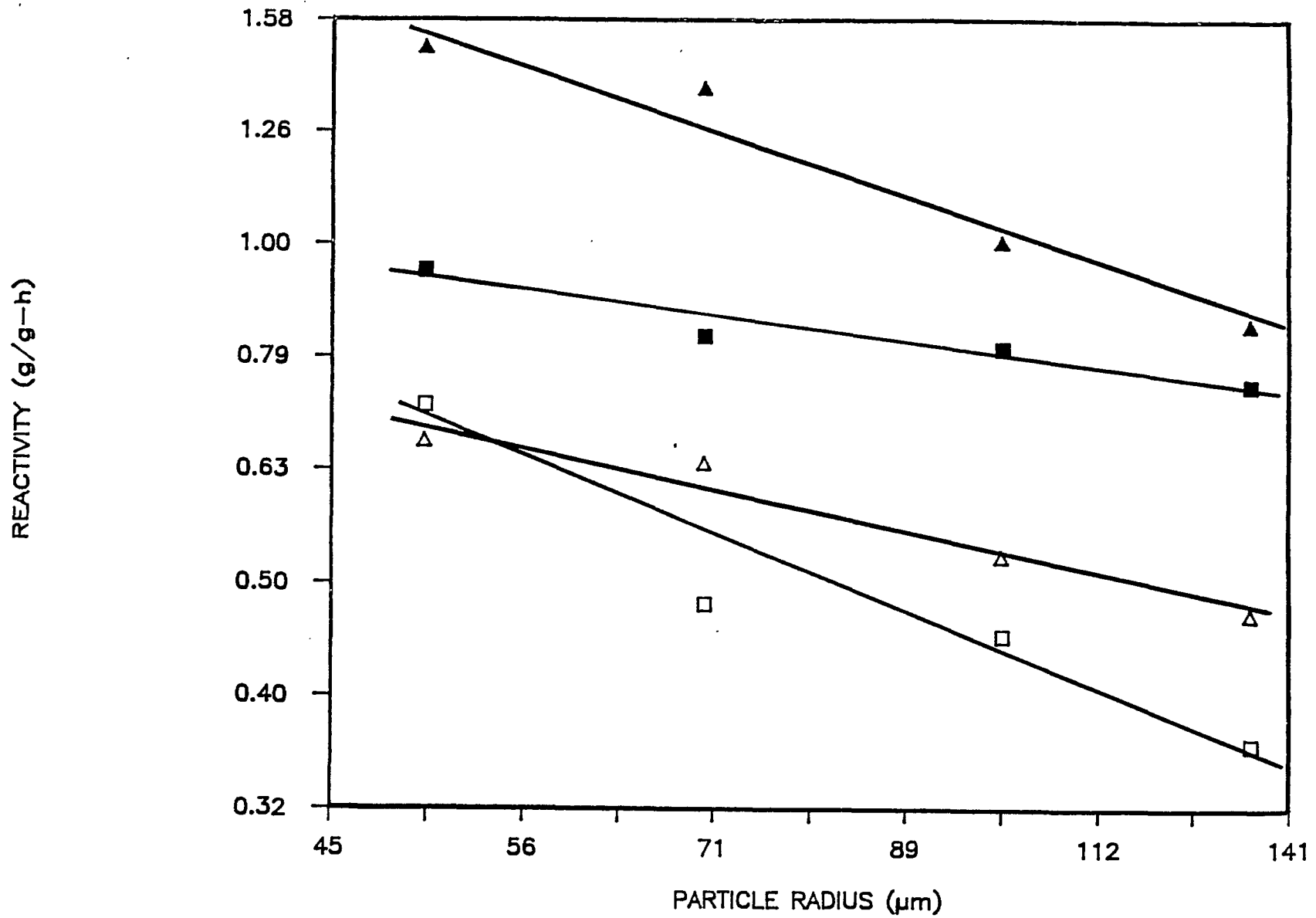


Figure 2. Analysis of char reactivity as a function of particle size using logarithmic scales; ■ Canmore char; □ demineralized Canmore char; ▲ Mt. Klappan char; △ demineralized Mt. Klappan char.

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MERCURY INTRUSION VOLUME (mL/g)

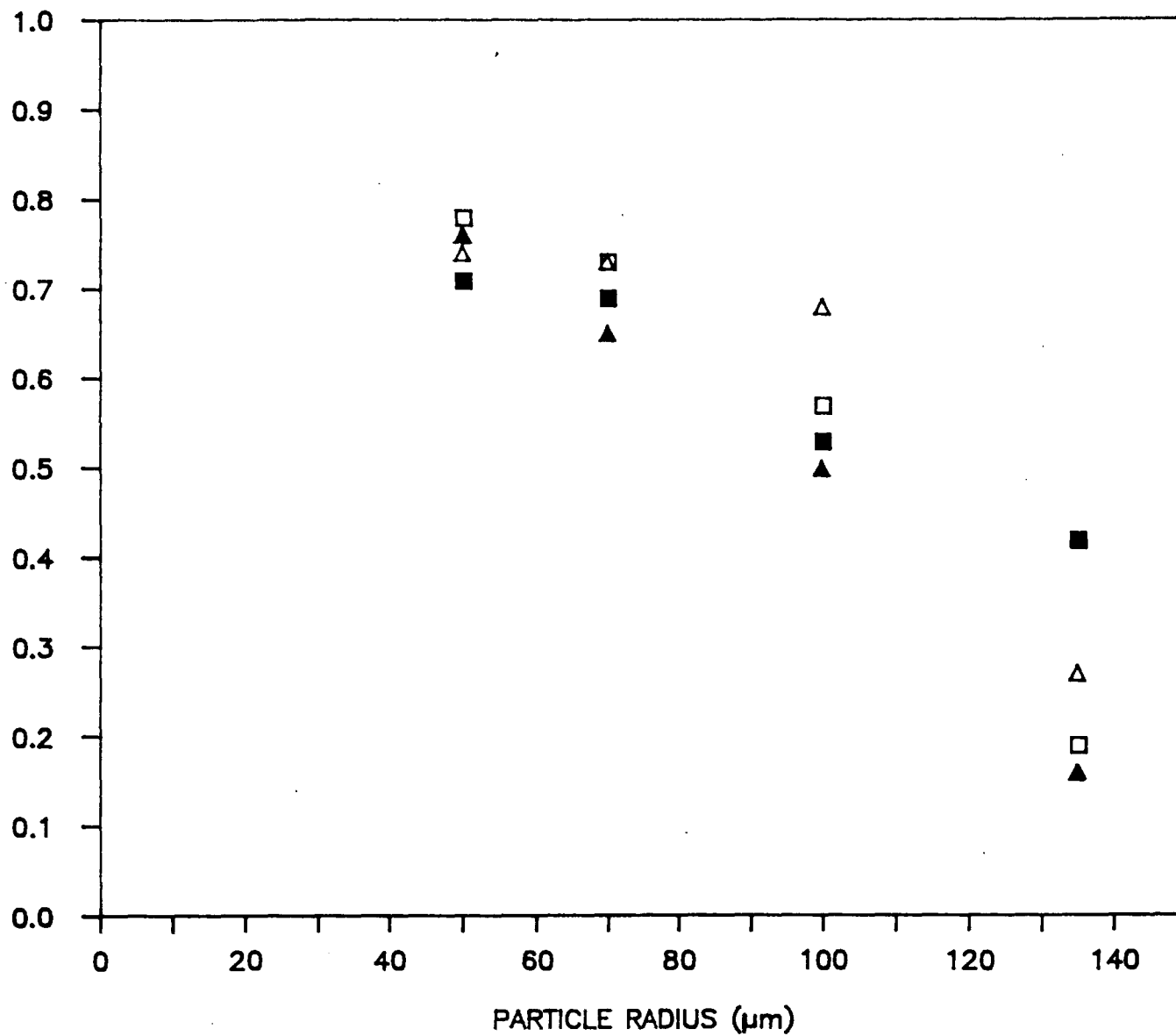


Figure 3. Effect of char particle size on mercury intrusion volume; ■ Canmore char; □ demineralized Canmore char; ▲ Mt. Klappan char; △ demineralized Mt. Klappan char.

PARTICLE RADIUS BY IMAGE ANALYSIS (μm)

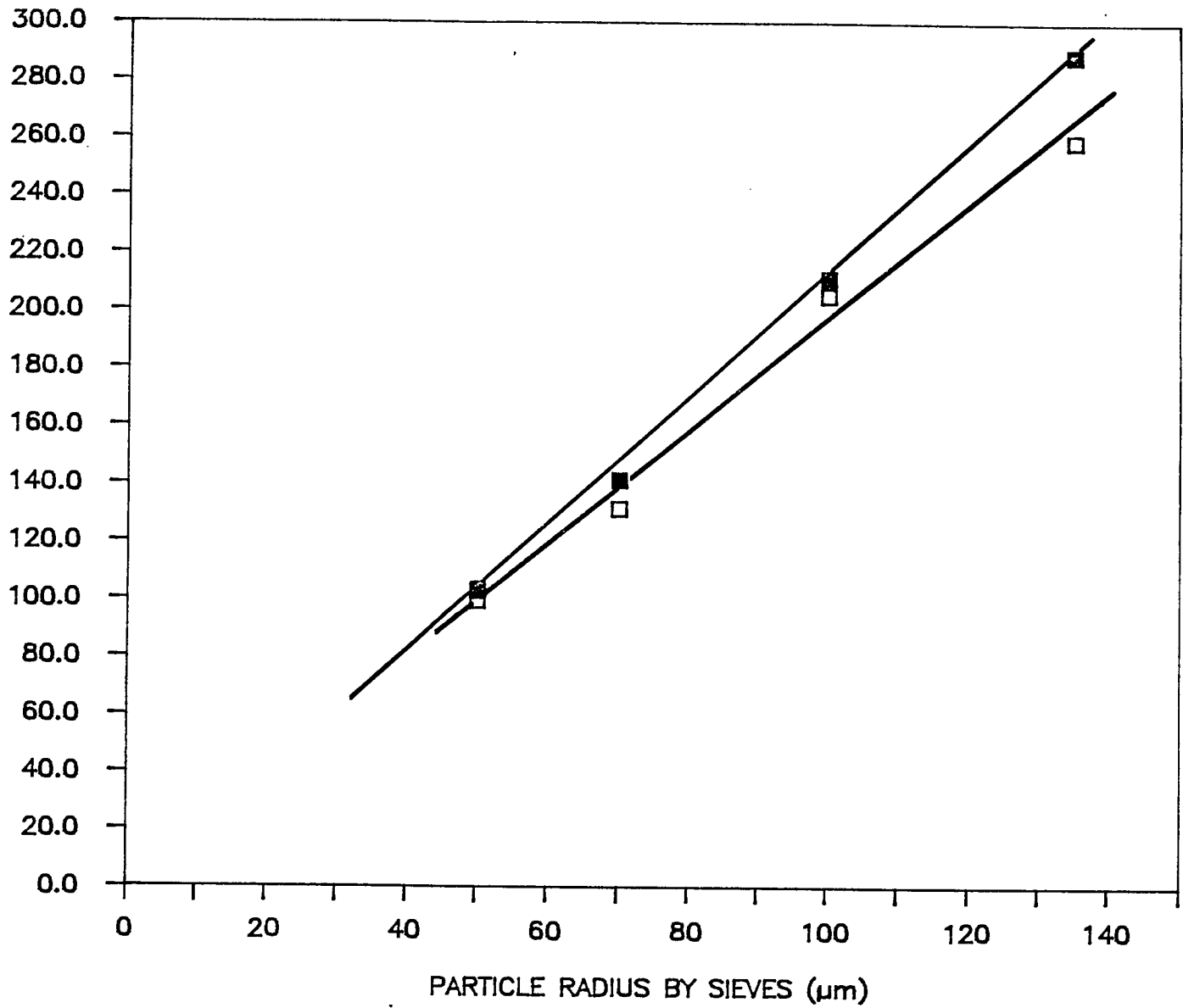


Figure 4. Relationship between particle radius measured by image analysis and sieve size; ■ Canmore char; □ demineralized Canmore char.