THE GASIFICATION REACTIVITY OF CARBONS - NEW DEVELOPMENTS

Eric M. Suuberg

Division of Engineering, Brown University, Providence, RI 02912

Keywords: Coal, carbon, surface area, porosity, gasification, combustion

Introduction

The reactions of chars (or "carbons") with oxidizing gases are among the most important of industrial reactions. Basic to utilization of any solid fuel, and important in processes ranging from activated carbon production to steel-making, they have been extensively studied for more than a century, e.g., 1,2. It is a tribute to the complexity of the processes involved that they have not yet yielded to intensive study, and a quantitatively predictive description of the phenomenon is not yet in hand. The difficulties in developing such a quantitative description are well-known. First, the materials from which the carbons are derived leave an indelible imprint on their character. Second, the temperature history of their preparation also has a significant impact. Modeling the complexity of the relevant pyrolysis processes still represents an imposing challenge (see the presentation by Serio et al. in this symposium). Third, the presence of small amounts of additional elements, serving as catalytic agents, influence both the course of carbon formation and subsequent gasification behavior. Finally, subtle aspects of combined phase and reaction behavior can drive the morphology of the carbons across a wide spectrum of characteristics (see the presentations by Hurt et al. and Winans et al. in this symposium). These morphological differences also play a key role in the subsequent reaction behavior of the carbons, as it is the ability of the oxidizing gases to gain access to the porosity in the carbon which determines some key aspects of the reaction process. Improvements in the quantitative description of these phenomena will require experimental examination of all of these processes at a greater level of detail. No single study will be able to provide all of the pieces, and progress will continue to be achieved through many fundamental examinations of various aspects of the processes. In this presentation, a key focal point will be the question of how porosity develops during gasification processes, and what this tells us about several of the above issues.

Patterns of Porosity Development

One useful new tool in the examination of this question is the use of NO as a model reactant. The reaction rates of carbons with NO are generally intermediate between the rates of carbon with oxygen on the one hand and those with CO_2 or steam on the other hand. Relatively few systematic studies of NO-carbon reactions have been undertaken; activation of carbons in NO is not of known commercial interest and the role of the carbon-NO reaction is of debated significance in practical combustion systems (they appear to clearly be of importance in fluidized beds, but probably of lesser importance in pulverized systems, except perhaps during reburning). Various aspects of the reaction have been recently reviewed[3].

Figure 1 shows that for gasification of a Wyodak coal-derived char in the intrinsic reaction rate regime, the development of *microporosity* follows a qualitatively similar pattern in three oxidizing gases (O_2, CO_2, NO), but there exist quantitative differences between the pattern in CO_2 and in the other gases. Experimental details have been provided elsewhere[4]. Characterization of porosity is here based upon traditional N_2 isotherm-derived quantities, but other adsorptives support the

Figure 1. Wyodak coal char surface area evolution in different oxidizing gases.
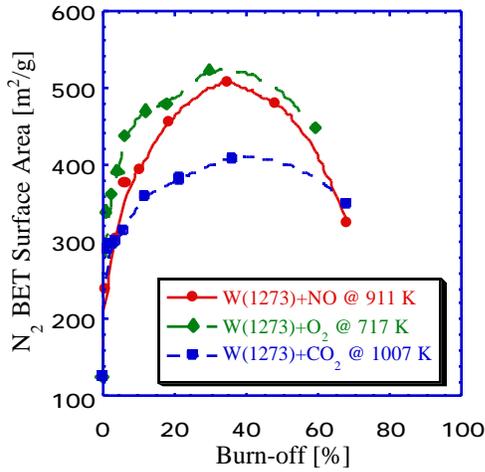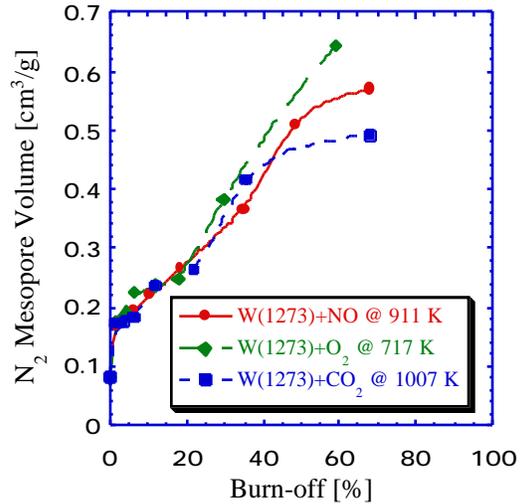

Figure 2. Wyodak coal char mesopore volume evolution in different oxidizing gases

conclusions[4]. The development of *mesoporosity* also follows a very similar pattern in all three gases, even quantitatively up to a certain point, see Figure 2. These results emphasize that some care is required in selection of data, and criteria, for drawing conclusions regarding the universality (or lack thereof) in a pattern of porosity development.

The so-called random pore models of gasification[5,6] have adopted the viewpoint that there is a single structural parameter which can be used to describe the relationship between conversion (extent of gasification) and porosity in the char. Figure 1 would require viewing this parameter as a a function of both starting material and gaseous environment. Figure 2, however, speaks to the possibility of viewing the structural parameter as a true material constant, at some level of approximation. Existence of a material-specific structural parameter is supported by results such as shown in Figure 3, illustrating development of porosity in a microcrystalline graphite, and Figure 4 showing development of porosity in a char derived from pine wood. Here, the data on porosity are shown as adsorption isotherms. Again, gasification conditions were selected so as to give comparable (apparently intrinsic) rates in all gases.

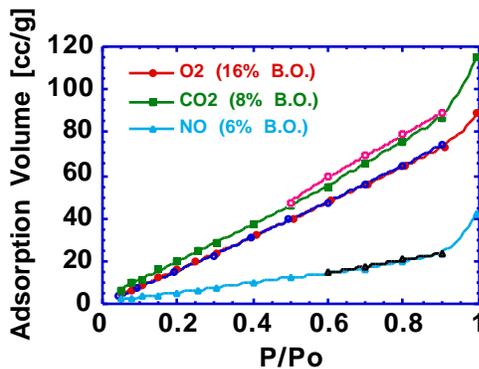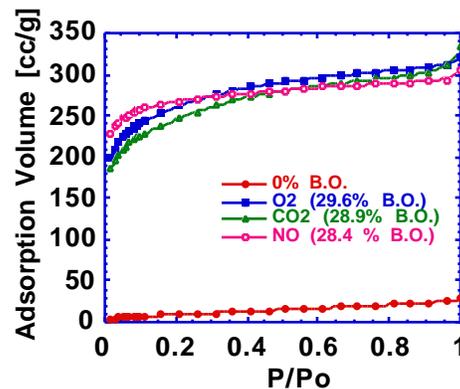**Figure 3. N_2 isotherms for graphite gasified in three gases (open points- desorption).**

Figure 4. N_2 isotherms for pine char reacted in three gases (adsorption isotherms).

These two cases represent extremes of behavior observed in many other materials. The graphite sample starts with virtually no porosity (the isotherm is at the bottom of the figure) and develops only fairly large-scale porosity (meso- and macroporosity), consistent with pitting of the surface. This is seen in Figure 3 as an increase in slope of the isotherms in the mid- to high- range of P/P_o, and this slope increases with burn-off. On the other hand, the char derived from pine shows a dramatic upward shift with burn-off of the isotherms in the low P/P_o range, indicating opening of microporosity. There are only modest change in meso- and macroporosity. The isotherms for the Wyodak material described in Figures 1 and 2 can be viewed as a composite of these two behaviors, consistent with the development of both types of pores.

It is clear from the above that the nature of activation is, to a first approximation, a property of the material and not of the reactant gas. The great importance of starting material is well known to those concerned with activated carbons. The reasons for these differences in porosity development patterns are not, however, entirely understood in all cases. It is fairly certain that the graphite cannot develop microporosity because of the locus and nature of the attack on its surface - the oxidizing gases are known to attack edge atoms, dislocations, etc., and this can only happen where the gases have access to such sites on the external surface. The pine char has a highly disordered structure to begin with, and a great deal of porosity, providing reactant gases access to its interior. Some of the dramatic increase in micropore volume in Figure 4 is an artifact of the well-known problem of activated diffusion of nitrogen at the low temperatures of measurement of the isotherms, but a large part is not, and there appears to be true development of both microporosity (and some mesoporosity). Does this require penetration of the reactant gases on the micropore size scale, as has been often suggested? It is unclear at the present time.

There can be no doubt that catalysis can play an important role in influencing the course of the observed processes. Figures 5 and 6 illustrate the mesopore size distributions observed after gasification of the Wyodak char in its original and demineralized states. The pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) method, corrected for micropore volumes[7]. This type of calculation is often criticized on various theoretical grounds, but the qualitative conclusions are very clear. The original Wyodak char, which is known to contain an abundance of catalytic mineral matter, develops very similar mesoporosity in all three gases (consistent with Figure 2). After demineralization, there is little mesoporosity development over the same range of burn-off. It is believed that it is the catalyst particles which in some manner dictate the development of the mesoporosity in the original sample, a conclusion consistent with the limited literature on this topic[8].

The above results notwithstanding, the results of Figure 1 show, as does much of the literature on activation of carbons, that the development of porosity during reaction of carbons in different gases can show distinct patterns, even if the reaction rates are closely matched, e.g., ref. 8. The results of Figures 3 through 6 appear to directly contradict a conclusion that CO_2 and O_2 will necessarily involve a very different pattern[8], but it is important to note that sometimes differences emerge only at higher burn-offs. Again, the reasons for the initial similarity and subsequent divergence are not yet understood. What does appear to be clear is that the differences are not an artifact of the choice of adsorptive used for examining porosity - both nitrogen and CO_2 isotherms offer similar conclusions. The other conclusion which may be drawn is that the simple, empirical porosity development models cannot yet handle this issue.

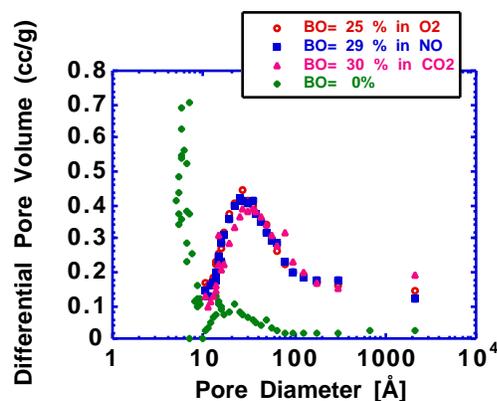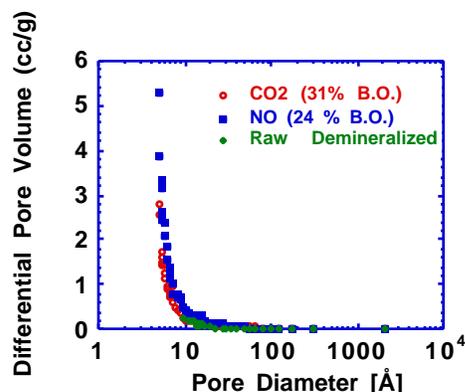**Figure 5. Pore size distributions for Wyodak char gasified in three gases.**

Figure 6. Pore size distributions for demineralized Wyodak char gasified in NO and CO_2.

Figure 5 legend:
- BO= 25 % in O2
- BO= 29 % in NO
- BO= 30 % in CO2
- BO= 0%

Figure 6 legend:
- CO2 (31% B.O.)
- NO (24 % B.O.)
- Raw Demineralized

Annealing

In the gasification and combustion literature, there is a well-established pattern of decrease in reactivity with increase in heat treatment temperature[9-19]. This phenomenon has often been termed annealing, on the basis that heat treatment "heals" the surface, removing the imperfections that constitute the main active sites. We have empirically modeled the process as involving an extension of high-temperature pyrolysis phenomena. The activation energy distributions characteristic of pyrolytic release of hydrogen merge with the activation energy distributions characteristic of graphitization. The distributed activation energy approach has been quite successful in predicting the changes in reactivity with heat treatment[12,20].

What has remained unclear is what physical factors are most important in determining the change in reactivity with heat treatment. Is the phenomenon tied to the gradual perfecting of aromatic structure, associated with the growth of condensed aromatic structures? Success has been achieved in correlating reactivity with hydrogen remaining in the structure[21]. Or is the loss of active sites mainly attributable to a loss of surface area with heat treatment? Both factors are sure to contribute to differing extents in different situations. In some cases, loss of catalyst or catalyst dispersion has also been cited.

The simple picture of reactivity loss with heat treatment is further complicated by several recent findings. First, there is the observation that annealing does not proceed at the same rate with respect to NO reactivity as it does with respect to oxygen reactivity[3]. In the case of NO, the annealing of a phenolic char could be entirely explained on the basis of surface area changes, whereas in the case of oxygen, there was an effect beyond surface area change involved. Another issue which has received attention recently is "memory loss" in gasification. As gasification conversion increases, differences in reactivity attributable to differences in heat treatment tend to disappear[11,22]. The effect has been attributed to selective burn-off of less ordered material early in the process, leaving behind increasingly similar more ordered and less reactive residues as conversion increases. What occurs is, however, not so clear when data on active site concentration variations with burn-off are considered. Figure 7 shows these trends in a phenolic resin char, in which active surface area (ASA) was determined by oxygen chemisorption[23]. As burn-off increased, the more highly heat treated char approached the less highly heat treated char in both

total surface area (TSA) and ASA. Meanwhile, the 573 K oxygen gasification reactivities of the samples slowly approached one another, in the usual fashion. What this means is that by one measure of structure and reactivity, the highly heat treated sample is becoming more reactive with burn-off. By the other measure, the less heat treated sample is declining in reactivity, while the more highly heat treated is remaining more or less the same. Clearly these results call into question the assay of ASA by oxygen chemisorption, and its significance with respect to high temperature gasification rates. But these results also suggest that the penetration of porosity by the oxygen reactant may be quite different in different reaction regimes; in the low temperature chemisorption regime, the oxygen reaches different porosity than in the higher temperature regime. This is, in fact, the basis of an exciting new carbon activation process being developed by AFR, Inc.[24].

Figure 8 shows that the more highly heat treated char develops a larger porosity than does the less heat treated char (again relying on a BJH-type pore size distribution analysis). The N_2 surface areas of these two samples are within about 15% of each other. Thus it seems possible that the

Figure 7. Reactivity and ASA variation in phenolic resin chars heat treated for 2 hours at indicated temperatures.
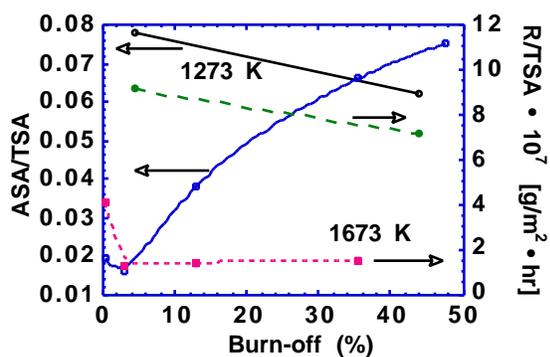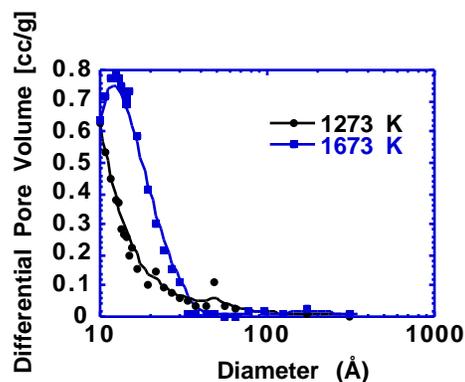
Figure 8. Pore size distributions for chars of Fig. 7, after approx. 20% burn-off in oxygen.

very different ASA behaviors are a consequence of the creation of more large porosity, in the case of the 1673 K char, and may not really be a good indicator of truly available ASA at high temperatures.

Surface Area and Reactivity

It has been recognized for quite some time that the rate of gasification of a carbon should in some way be related to its surface area. The above data and discussion have perhaps already raised concerns regarding how difficult it might be to assess the correct surface areas. Historically, two main methods have been employed for measuring the areas. One involves the use of nitrogen isotherms and the BET equation, and the other involves use of carbon dioxide isotherms and some form of the Dubinin-Radushkevich equation. The relative merits of both methods have been debated for some time. While it is true that activated diffusion barriers are sometimes a problem for N_2 adsorption at liquid nitrogen temperatures, the importance of this issue has perhaps been overplayed. Carbon dioxide is, on the other hand, often unable to interrogate the larger micropores[7]. It has thus been recommended that a combination of both probes be used to avoid

drawing false conclusions[7]. We have recently examined a number of adsorptives on the same chars, and concluded that there was no particular advantage to use of carbon dioxide over nitrogen[4].

Reactivity data for the Wyodak chars are shown in Figure 9, again using the three main oxidizing gases of this study. All of these data show an increase in reactivity per mass of remaining carbon, with burn-off (note that the behavior in this case was only tracked to 70% burn-off). The question of whether the reactivities could be normalized by surface areas was then examined. Figure 10 shows the results of normalization by BET surface areas. The only special feature of this normalization is that the reactivity at 1% burn-off was taken as the reference, in order to avoid issues related to severe activated diffusion limitations leading to apparently low BET areas at near zero burn-off. Thus if surface area truly normalizes reactivity, a horizontal line should be obtained at unity. Such is very nearly the case in oxygen and in carbon dioxide, but not in NO. Still, caution must be exercise in concluding that reactive gases can reach all of the available micropore surface areas in the cases of oxygen and carbon dioxide. It was suggested in connection with Fig. 5 that the main locus of reaction may be catalyst particles. In such a case, an apparent correlation of

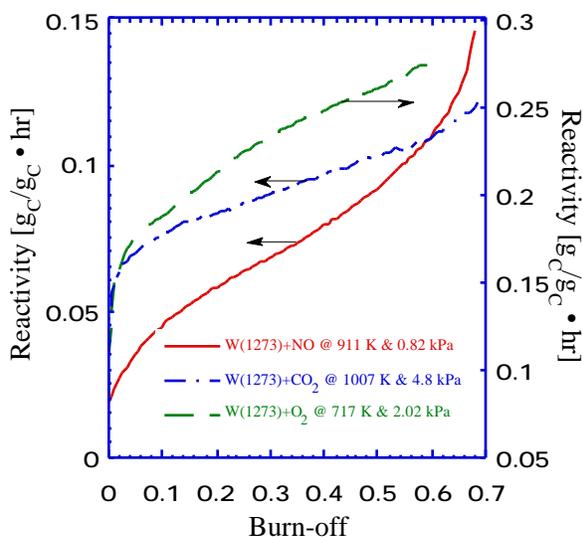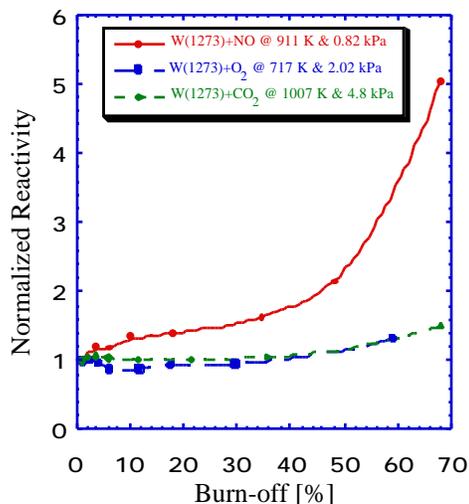**Figure 9. Reactivity of Wyodak char in different oxidizing gases.**   **Figure 10. Normalized reactivities of Wyodak char.**

reactivity with surface area may be indirect; catalyst area may correlate with micropore area for some reason. In any case, a correlation with surface area might actually only be a correlation with numbers of micropores, and reactants may be unable to use any more than the mouths of the micropores. Suggestions that micropores might not be fully utilized in reaction are numerous[5,16,25,26].

The case of NO reactivity was particularly interesting. In the case of this reactant, the normalization appeared to be poor. Examined more closely, the curve for NO does, however, show a period of relatively constant reactivity per unit of surface area. This has been taken to indicate that the normalization reactivity per unit area (at 1% burn-off) was actually too low, in this case by about 50%, since the period of constant reactivity occurs at a normalized value of about 1.5 . This in turn indicates that the microporosity initially present was not all available for reaction, and was only opened up by 10% burn-off. Beyond 40% burn-off, the curve begins to rise sharply once again. This is further indication that the original normalization was based upon the wrong (too high)

surface area. Only as the microporosity is opened up (becomes wider) does NO gain greater access to the surface. This was verified by sharp changes in the pore size distributions in this range of burn-offs. Thus, the use of BET or DR surface areas to normalize reactivities is of little fundamental significance, and should be approached with great caution.

Summary
Results have been obtained for a wide range of carbons, which suggest that the development of porosity is most strongly dependent upon the nature of the starting material. Gasification environment can play a role in porosity development, as may the presence of catalysts. Annealing of the carbon influences its porosity and therefore, accessibility of reactant gases. Surface areas for reaction of gases with carbons are a useful concept, but the methods presently used to normalize reactivities must be viewed as essentially empirical. There is evidence to suggest that micropore surfaces are not available for reaction.

Acknowledgment

References
1. Walker, P.L., Jr.; Rusinko, F., Jr.; Austin, L.G. *Adv. Cat.***1959**, *XI*, 133.
2. Essenhigh, R.H. in *Chemistry of Coal Utilization, Second Supplementary Volume*, M. Elliott, Ed., Chap. 19, Wiley, 1981.
3. Aarna, I.; Suuberg, E.M. *Fuel*, **1997**, *76*, 475.
4. Aarna, I.; Suuberg, E.M. *27th Symp. (Int.) on Comb.*, in press, 1998.
5. Gavalas, G.R. *AIChEJ*, **1980**, *26*, 577.
6. Bhatia, S.K.; Perlmutter, D.D. *AIChEJ*, **1980**, *26*, 379.
7. Rodríguez-Reinoso, F.; Linares-Solano, A., in *Chemistry and Physics of Carbon*, *Vol. 21*, P. A. Thrower, Ed., p. 1, Dekker, New York, 1989.
8. Rodriguez-Reinoso, F.in *Fundamental Issues in Control of Carbon Gasification Reactivity*, J. Lahaye, P. Ehrburger, Eds. p. 533 , Kluwer Academic, Dordrecht, 1991.
9. van Heek, K.H.; Mühlen, H.J. *Fuel*, **1985**, *64*, 1405.
10. Duval, X. *Ann. de Chem., 12th Ser.*, **1955**, *10*, 58.
11. Senneca, O.; Russo, P.; Salatino, P.; Masi, S. *Carbon*, **1997**, *35*, 141.
12. Suuberg, E.M. in *Fundamental Issues in Control of Carbon Gasification Reactivity*, J. Lahaye, P. Ehrburger, Eds. p. 269, Kluwer Academic, Dordrecht, 1991.
13. Serio, M. A.; Solomon, P.R.; Bassilakis, R.; Suuberg, E.M. *ACS Div. Fuel Chem. Prepr.***1989**, *34(1)*, 9.
14. Beeley, T.; Crelling, J.; Gibbins, J.; Hurt, R.; Lunden, M.; Man, C.; Williamson, J.; Yang, N. *26th Symp (Int.) on Comb.* p. 3103, The Combustion Institute, Pittsburgh, 1996.
15. Jenkins, R.G.; Nandi, S.P.; Walker, P.L., Jr. *Fuel*, **1973**, *52*, 288.
16. Radovic, L.R.; Walker, P.L., Jr.; Jenknis, R.G. *Fuel*, **1982**, *62*, 849.
17. Gale, T.K.; Bartholomew, C.H.; Fletcher, T.H. *Energy Fuels*, **1996**, *10*, 766.
18. Kasaoka, S.; Sakata, Y.; Shimada, M. *Fuel*, **1987**, *66*, 697.
19. Sahu, R.; Levendis, Y.; Flagan, R.; Gavalas, G. *Fuel*, **1988**, *67*, 275.
20. Hurt, R.H.; Sun, J.K.; Lunden, M. *Comb. Flame*, **1998**, *113*, 181.
21. Charpenay, S.; Serio, M.A.; Solomon, P.R. *24th Symp (Int.) on Comb.* p. 1189, The Combustion Institute, Pittsburgh, 1992.
22. Anxustegi, M.M.; Calo, J.M.; Hurt, R.H.; Shim, H. S. *Proc. Eurocarbon '98*, p. 675, GFEC, 1998.
23. Suuberg, E.M.; Wójtowicz, M.; Calo, J.M. *Carbon*, **1989**, *27*, 431.
24. Wójtowicz, M.; Markowitz, B.L.; Simons, G.; Serio, M.A. *ACS Div. Fuel Chem. Prepr.***1998**, *43*, 585.
25. Hurt, R.H.; Sarofim, A.F.; Longwell, J. *Fuel*, **1991**, *70*, 1079.
26. Dutta, S.; Wen, C.Y.; Belt, R.J. *Ind. Eng. Chem. Proc. Des. Dev.***1977**, *16*, 20.