$$H_1(\lambda, \nu) = \frac{H_{D_1} + \nu(H_{D_1}^2 + H_{D_2}^2)}{(1 + \nu H_{D_1})^2 + (\nu H_{D_2})^2}$$

$$H_2(\lambda, \nu) = \frac{H_{D_2}}{(1 + \nu H_{D_1})^2 + (\nu H_{D_2})^2}$$

$$H_{D_1}(\lambda) = \lambda\left(\frac{\sinh 2\lambda + \sin 2\lambda}{\cosh 2\lambda - \cos 2\lambda}\right) - 1$$

$$H_{D_2}(\lambda) = \lambda\left(\frac{\sinh 2\lambda - \sin 2\lambda}{\cosh 2\lambda - \cos 2\lambda}\right)$$

Accordingly

$$Y_T'(i\beta) = \sqrt{\frac{V^2}{4D_L^2} + \frac{i\beta}{D_L} + \frac{\gamma}{mD_L}[H_1(\lambda, \nu) + iH_2(\lambda, \nu)]}$$

The square-root is evaluated by writing the quantity under the square-root sign on polar form

$$Y_T'(i\beta) = \sqrt{r'(\cos\theta + i\sin\theta)}$$

where

$$r' = \sqrt{x'^2 + y'^2}$$

$$\theta = \arctan\frac{y'}{x'}$$

$$x' = \frac{V^2}{4D_L^2} + \frac{\gamma}{mD_L}H_1$$

$$y' = \frac{\beta}{D_L} + \frac{\gamma}{mD_L}H_2$$

Applying de Moivre's theorem we get

$$Y_T'(i\beta) = r'^{\frac{1}{2}}\left(\cos\frac{\theta}{2} + i\sin\frac{\theta}{2}\right)$$

Using trigonometric formulas we find that

$$\cos\frac{\theta}{2} = \sqrt{\frac{1 + \frac{x'}{r'}}{2}}$$

$$\sin\frac{\theta}{2} = \sqrt{\frac{1 - \frac{x'}{r'}}{2}}$$

It follows that

$$Y_T'(i\beta) = \sqrt{\frac{r' + x'}{2}} + i\sqrt{\frac{r' - x'}{2}} \tag{25}$$

We are now ready to obtain

$$\begin{aligned} Re[e^{i\beta t}\tilde{u}(z, i\beta)] &= Re\left\{\frac{1}{i\beta}\exp\left[i\beta t - z\left(\sqrt{\frac{r'+x'}{2}} + i\sqrt{\frac{r'-x'}{2}}\right)\right]\right\} \\ &= Re\left\{-\frac{i}{\beta}\exp\left(-z\sqrt{\frac{r'+x'}{2}}\right)\left[\cos\left(\beta t - z\sqrt{\frac{r'-x'}{2}}\right) + i\sin\left(\beta t - z\sqrt{\frac{r'-x'}{2}}\right)\right]\right\} = \frac{1}{\beta}\exp\left(-z\sqrt{\frac{r'+x'}{2}}\right) \\ &\quad \sin\left(\beta t - z\sqrt{\frac{r'-x'}{2}}\right) \end{aligned}$$

and

$$I_4 = \frac{1}{\pi}\int_0^\infty \exp\left(-z\sqrt{\frac{r'+x'}{2}}\right)\sin\left(\beta t - z\sqrt{\frac{r'-x'}{2}}\right)\frac{d\beta}{\beta} \tag{26}$$

From (21), (22) and (26) making the substitution $\beta = \sigma\lambda^2$ we finally obtain

$$\begin{aligned} u(z, t) &= C(z, t)/C_o \\ &= \frac{1}{2} + \frac{2}{\pi}\int_0^\infty \exp\left(\frac{Vz}{2D_L} - z\sqrt{\frac{\sqrt{x'(\lambda)^2 + y'(\lambda)^2} + x'(\lambda)}{2}}\right) \\ &\quad \sin\left(\sigma\lambda^2 t - z\sqrt{\frac{\sqrt{x'(\lambda)^2 + y'(\lambda)^2} - x'(\lambda)}{2}}\right)\frac{d\lambda}{\lambda} \end{aligned} \tag{27}$$

with

$$x'(\lambda) = \frac{V^2}{4D_L^2} + \frac{\gamma}{mD_L}H_1$$

$$y'(\lambda) = \frac{\sigma\lambda^2}{D_L} + \frac{\gamma}{mD_L}H_2$$

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# Hydrodesulfurization of Benzo[b]naphtho[2,3-d]thiophene Catalyzed by Sulfided CoO-MoO$_3$/$\gamma$-Al$_2$O$_3$: The Reaction Network

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The need for clean-burning fuels and the depletion of petroleum reserves are dictating the development of catalytic hydrodesulfurization processes for the heaviest petroleum fractions and for coal-derived liquids. These feedstocks require processing conditions much more severe than those used for

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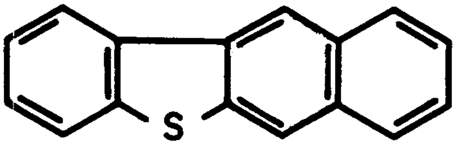
petroleum distillates (Gates et al. 1979). The emerging technology demands desulfurization of relatively unreactive 3- and 4-ring aromatic compounds like dibenzothiophene and benzo[b]naphtho[2,3-d]thiophene (referred to as benzonaphthothiophene):



As part of a systematic study of the reactivities of these and related compounds under high-pressure reaction conditions that are representative of industrial practice, we reported a reaction network for dibenzothiophene hydrodesulfurization (Houalla et al. 1978) and rates of reaction comparing 1-, 2-, 3-, and 4-ring compounds (Nag et al. 1979) and methyl-substituted dibenzothiophenes (Houalla et al. 1980). Continuing the study, we report here the resolution of the reaction network involving benzonaphthothiophene and hydrogen. As before, the catalyst was a typical commercial, sulfided CoO-MoO$_3$/γ-Al$_2$O$_3$ operated under conditions of practical interest with liquid-phase reactants.

## BATCH REACTOR EXPERIMENTS

A one-liter high-pressure batch reactor (Autoclave Engineers) was used; the design allowed charging of the catalyst after the reactants had been brought to reaction temperature, virtually eliminating any heat-up period which would prevent elucidation of isothermal kinetics from the conversion data (Shih et al. 1977).

The catalyst was particles ($1.5 \times 10^{-4}$ m diameter) of CoO-MoO$_3$/γ-Al$_2$O$_3$ (American Cyanamid HDS 16A), ($2 \times 10^{-4}$ kg), which was externally sulfided at 673 K with 10 vol% H$_2$S in H$_2$ at atmospheric pressure for two hours, prior to being charged to the reactor. The reactant solution ($3.2 \times 10^{-4}$ m$^3$) contained 0.24 wt% benzonaphthothiophene—synthesized by the method of Campaigne and Osborn (1968)—in $n$-hexadecane (Humphrey Chemical Company, redistilled), or one of the organic products of its conversion. This solution was saturated with hydrogen, providing a large stoichiometric excess of this reactant. The reactor was operated at 70 atm and 573 K. The agitator speed was about 1,500 rev/min. Calculations and comparisons with data obtained in complementary experiments showed that the interphase and intraparticle mass transfer resistances were negligible.

## PRODUCT ANALYSIS

Product samples were drawn periodically from the reactor and analyzed with an Antek 440 L gas chromatograph (glc) equipped with a flame ionization detector and a column packed with methyl silicone fluid (with basic sites deactivated) on 100-120 mesh Supelcoport (GP 3%, SP-2100 DB, Supelco). Separate analyses to determine sulfur-containing compounds in the product were carried out with a Perkin-Elmer 3920B glc, equipped with a sulfur-specific detector. Details of the gas chromatographic analysis are as described previously (Houalla et al. 1978).

For qualitative identification of the aromatic products, tricarbonyl chromium complexes of the products were synthesized using chromium hexacarbonyl, according to the procedure of Nicholls and Whiting (1959). The product solution was first diluted with $n$-heptane ($n$-C$_7$:$n$-C$_{16}$ = 1:2 by volume). After about 10 hours' heating with chromium hexacarbonyl under reflux at 443 K, a yellow solution was obtained. This solution was passed through an alumina (Fisher, 6% water) column. The hydrocarbon solvent and uncomplexed aromatics were eluted with $n$-pentane. With a flow of 1:9 methylene chloride: $n$-pentane solution, two yellow bands were separated, and one was eluted.

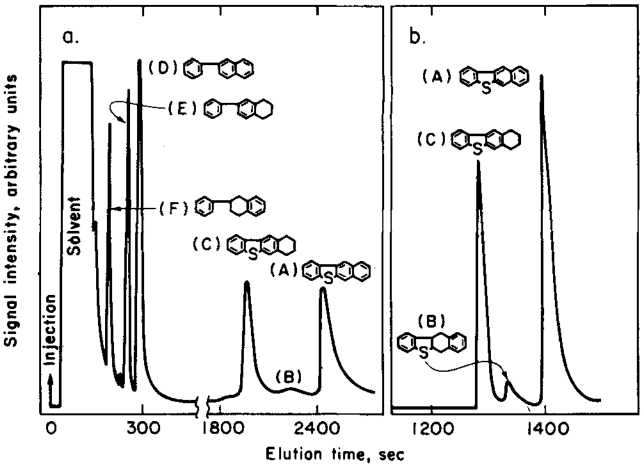


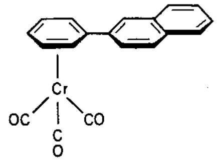
**Figure 1. Gas chromatographic analysis of the products of hydrodesulfurization of benzo[b]naphtho[2,3-d]thiophene at 573 K and 70 atm. a) The full organic product spectrum determined with a flame ionization detector; b) The sulfur-containing organic compounds, determined with a sulfur-specific detector (details in the text).**

The compound in this eluted band, after recrystallization from $n$-hexane, was identified as the tricarbonyl chromium complex of the compound designated **E** (Complex **E**) in the product chromatogram (Figure 1). The second band was eluted with 1:5 methylene chloride: $n$-pentane solution and found to contain a mixture of products. These were separated by repeated recrystallization from $n$-hexane and $n$-pentane. They were identified as the tricarbonyl chromium complexes of the compounds designated **D** and **F** (Complex **D**, Complex **F**) in Fig. 1. The products were identified by proton NMR spectroscopy, with the results described in the following section. Spectra were taken using a Perkin-Elmer R12B 60MHz ($^1$H) spectrometer, with CDCl$_3$ as solvent, and tetramethylsilane as external reference.

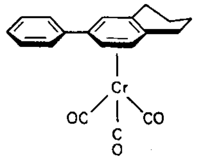
## RESULTS

Figure 1 shows typical chromatograms indicating the product spectrum from a sample which had experienced a high conversion (about 95%). Figure 1b is the chromatogram obtained with the sulfur-specific detector. Peak **C** (Figures 1a and 1b) represents the major sulfur-containing product, which was formed from the beginning of the batch kinetics experiment (Figure 2) and is therefore identified as a primary product. It has been shown to be 7,8,9,10-tetrahydrobenzo[b]naphtho[2,3-d]thiophene (referred to as 7,8,9,10-tetrahydrobenzonaphthothiophene) on the basis of the comparison of its retention time and peak shape with those of the authentic sample, synthesized by the method of Campaign and Osborn (1968).

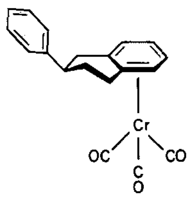
Isolation of the tricarbonyl chromium complexes of products **D**, **E**, and **F** and analysis by proton NMR led to identification of the following three compounds:



Complex of **D**



Complex of **E**



Complex of **F**

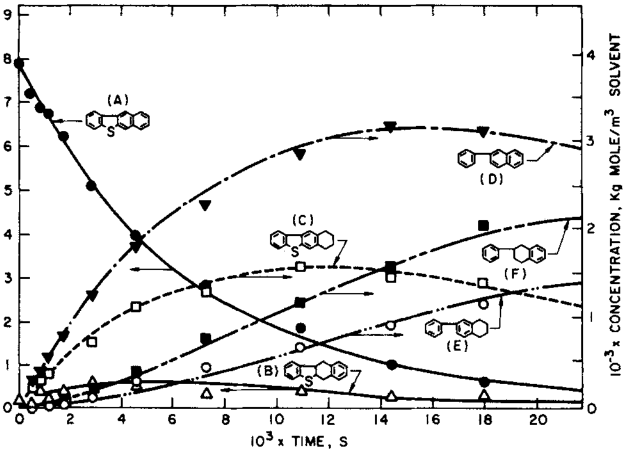


**Figure 2. Conversion of hydrogen and benzo[b]naphtho[2,3-d]thiophene in the presence of sulfided $CoO$-$MoO_3$/$\gamma$-$Al_2O_3$ in a batch reactor at 573 K and 70 atm. The solvent was *n*-hexadecane. The curves are the predictions of the reaction network model summarized in Figure 3.**

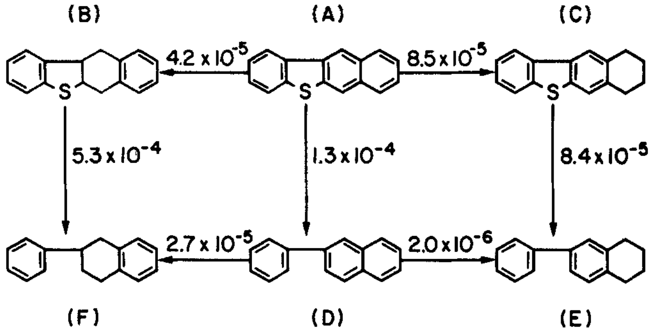


**Figure 3. Conversion of benzo[b]naphtho[2,3-d]thiophene and hydrogen in the presence of sulfided $CoO$-$MoO_3$/$\gamma$-$Al_2O_3$ at 573 K and 70 atm: the reaction network. Each reaction is approximated as first order in the organic reactant; the numbers next to the arrows are the pseudo first-order rate constants in cubic meters per kilogram of catalyst per second.**

The structural assignments based on the NMR spectra (Sneeden 1975) were made as follows: Complex **D** had no protons other than aromatic protons (i.e., a horizontal baseline at $\tau \geq 4.5$), and the integrated proton ratio between the complexed ($\tau 3.8 - 4.5$) and uncomplexed ($\tau 1.7 - 2.5$) rings was 5:7, as expected from the above structure. No other complexes of 2-phenylnaphthalene could be isolated, in agreement with the fact that only one tricarbonyl chromium complex was obtained from a direct reaction of 2-phenylnaphthalene with chromium hexacarbonyl, giving a NMR spectrum identical with that of Complex **D**.

Complex **E** presented a NMR spectrum indicating one uncomplexed ring ($\tau 2.1$, 5H), one complexed ring ($\tau 4.0$, 3H), and two bands representative of methylene protons ($\tau 6.9$ and 7.9 for methylenes $\alpha$ and $\beta$ to the complexed ring, respectively), each corresponding to 4H. The structure assigned to Complex **E** is the only one in agreement with this spectrum. The aromatic part of the spectrum of Complex **F** was similar to that of Complex **E**—one uncomplexed ring ($\tau 2.25$, 5H) and one complexed ring ($\tau 4.3$, 4H)—but the high-field part of the spectrum showed a different pattern, namely three absorption bands with a proton ratio 4:1:2 (at $\tau 6.8$, 6.9, and 7.6, respectively), corresponding to four methylene hydrogens, to one methine hydrogen, and to two hydrogens on a methylene group which is $\beta$ to the complexed ring. There is only one structure in accord with the spectrum, namely the one drawn above for Complex **F**.

Samples of the purified complexes of **D**, **E**, and **F** were allowed to decompose in acetone, regenerating the hydrocarbons. These were analyzed by glc, and gave the peaks corresponding to **D**, **E**, and **F**, respectively.

The identification of the structure **E** is confirmed, since **E** appeared as the principal primary product in a separate reaction experiment, with **C** as the organic reactant. Experience with similar sulfur-containing compounds under the same reaction conditions had already led us to expect that the main product of the reaction of **C** should be the desulfurization product, not the hydrogenation product.

The other principal product in the conversion of benzonaphthothiophene, namely **F** (Figure 1), could be obtained as a secondary product by hydrogenation of **D** and also (as in the case of **E**), by hydrodesulfurization of the appropriately prehydrogenated sulfur-containing compound, which we now ascribe to peak **B** (Figure 1). **B** was always a minor intermediate, which is not surprising in view of the suggested structure, since when one of the rings next to the one containing sulfur is reduced, the compound is expected to be much more susceptible to hydrodesulfurization (Houalla et al. 1978). Like **C**, **B** is apparently also a primary product, although an absolute statement is prohibited because of the appearance of **B** as impurity in **A** as well as the scatter in concentration data near time zero (Figure 2). Further evidence for this assumption is found in the dibenzothiophene network (Houalla et al. 1978).

Combining the foregoing product identifications with the recognition of which products were primary and which were secondary (Figure 2) allows us to state the qualitative reaction network involving benzonaphthothiophene and hydrogen, as shown in Figure 3.

## DISCUSSION

The appearance of a hydrocarbon (2-phenylnaphthalene) and two partially hydrogenated sulfur-containing compounds (one or the other rings of the naphthalenic part of the molecule being saturated) as primary products indicates a similarity between the network for benzonaphthothiophene and that for dibenzothiophene (Houalla et al. 1978). The striking difference is that, in the case of dibenzothiophene, the hydrogenation prior to sulfur abstraction is almost negligibly slow in comparison with the parallel hydrodesulfurization. It is three orders of magnitude slower (provided that the $H_2S$ concentration is low), whereas the parallel hydrogenation and hydrodesulfurization of benzonaphthothiophene proceed at nearly equal rates. The maxima in the concentration-time plots for the primary products (Figure 2) show that they are intermediates, undergoing conversion into hydrocarbons. Three primary products give rise to two secondary products, 2-phenyltetralin (**E**) and 6-phenyltetralin (**F**). In the experiments carried out with benzonaphthothiophene as the organic reactant, the three primary products and two secondary products gave a >98% mass balance; the reaction network shown in Figure 3 is, therefore, regarded as complete.

To test this model of the network, a few experiments were performed with the available primary products (7,8,9,10-tetrahydrobenzonaphthothiophene and 2-phenylnaphthalene) used instead of benzonaphthothiophene as the organic reactant. Otherwise, the procedures were the same as described above, except that carbon disulfide was added to the reaction mixture to maintain the sulfided state of the catalyst when 2-phenylnaphthalene was the reactant. The 7,8,9,10-tetrahydrobenzonaphthothiophene (**C**) gave 2-phenyltetralin (**E**) as a primary product. When experiments were carried out with 2-phenylnaphthalene (**D**), two primary products were formed, identified as 2-phenyltetralin (**E**) and 6-phenyltetralin (**F**), confirming the proposed network.

More complete kinetics data for hydrogenation of 2-phenylnaphthalene to 2-phenyltetralin and 6-phenyltetralin, suggesting that these primary reactions are reversible, are presented elsewhere (Sapre and Gates, 1980). It is known from the literature that the analogous naphthalene–tetralin reaction is reversible (Bhinde 1979). The reversible reactions are kinetically insignificant, however, for the benzonaphthothiophene conversion under the conditions of this work. They are, therefore, not included in the following analysis.

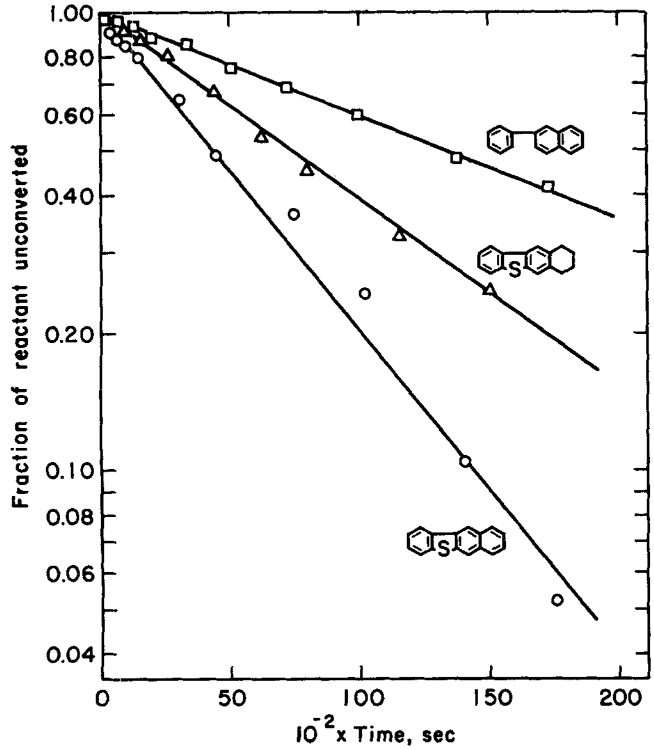


**Figure 4. Pseudo first-order kinetics of hydrodesulfurization and hydrogenation catalyzed by sulfided CoO-MoO$_3$/γ-Al$_2$O$_3$ in a batch reactor at 573 K and 70 atm. Each of the compounds shown was used separately as the organic reactant with hydrogen in a batch reactor. The conversion data were determined from the measured disappearance of reactant.**

The sulfur-containing product **B** was not commercially available and not easily synthesized, and no experiments were performed with this compound as the organic reactant. Since its concentration passed through a maximum (Figure 2), further reaction of **B** is apparent. In analogy with **C** it seems obvious that the desulfurized product obtained from **B** would be 6-phenyltetralin (**F**).

The conversion data for each of the organic reactants used separately can be represented well by pseudo first-order kinetics (Figure 4). Therefore, in determining a quantitative model of the reaction network, it was assumed that each reaction was first order in the organic reactant. The pseudo first-order rate constants were estimated from the full set of data determined in the experiments with benzonaphthothiophene feed, as follows: (1) The data of Figure 2 were smoothed by fitting spline functions using the IMSL subroutine ICSMOU. This program performs one-dimensional data smoothing by error detection, and is highly effective in smoothing a data set only mildly contaminated with isolated errors. (2) The smoothed data were used with equal weighting in the Carlton 2 program (Himmelblau et al. 1967) to determine best values of the rate constants. The values of the rate constants are given in Figure 3, and the conversion-time curves predicted from the model are shown in Figure 2. The experimental points shown in Figure 2 compare well with the model of the network.

TABLE 1. PSEUDO FIRST-ORDER RATE CONSTANTS, OBTAINED FROM SLOPES IN FIGURE 4.

| Reactant | Pseudo first-order rate constant, m$^3$/kg of catalyst·s |
|---|---|
| Benzonaphthothiophene | $1.6 \times 10^{-4}$ |
| 7,8,9,10-Tetrahydrobenzonaphthothiophene | $7.8 \times 10^{-5}$ |
| 2-Phenylnaphthalene | $3.3 \times 10^{-5}$ |

The pseudo first-order rate constants for the overall disappearance of each component, as obtained from the slopes of Figure 4, are summarized in Table 1. We cannot directly compare these rate constants with the corresponding values obtained in the network analysis, but the data are internally consistent: 7,8,9,10-tetrahydrobenzonaphthothiophene gave only one primary product, and hence the rate constant obtained from the network analysis ($8.4 \times 10^{-5}$ m$^3$/kg of catalyst·s) compares well with the pseudo first-order rate constant for overall disappearance ($7.8 \times 10^{-5}$ m$^3$/kg of catalyst·s). For benzonaphthothiophene and 2-phenylnaphthalene, the pseudo first-order rate constants for overall disappearance correspond approximately to the rate constants obtained in the network analysis for the fastest reaction involving that particular component. Exact agreement is not expected, however, since the reaction environments were different in the various experiments, and the competitive adsorption (inhibition) effects were not taken account of in the simple network model.

On the basis of experience in determining the full nonlinear kinetics, with inhibition effects, for the simpler dibenzothiophene hydrodesulfurization (Broderick and Gates, 1980), we infer that a much larger set of data (probably 100 times as many data points) would be required to determine, with comparable precision, full rate equations—with estimates of rate constants and inhibition (adsorption) parameters—for the whole set of reactions in the benzonaphthothiophene + hydrogen network.

The important result is that, in contrast to dibenzothiophene, benzonaphthothiophene experiences extensive hydrogenation accompanying hydrodesulfurization, even with Co-Mo/γ-Al$_2$O$_3$, the most selective of the available hydrodesulfurization catalysts. Consequently, hydrogen consumptions (and processing costs) will unavoidably be high when feedstocks have appreciable concentrations of 4-ring and larger sulfur-containing compounds. These results, in combination with earlier work (Houalla et al. 1978, Kilanowski et al. 1978), lead to the recommendation of the following approximations for modeling the hydroprocessing of heavy petroleum and coal-liquid feedstocks: The sulfur-containing compounds having three or fewer rings experience nearly stoichiometric hydrodesulfurization (hydrogenolysis without hydrogenation), at low H$_2$S concentrations (but hydrogen consumptions are higher at higher H$_2$S concentrations). The sulfur-containing compounds having four or more rings experience hydrogenation and hydrodesulfurization at roughly equal rates, giving products which experience further hydrogenation (and/or hydrodesulfurization—as the composition allows), again at roughly the same rates. This preliminary recommendation requires critical evaluation on the basis of further experimentation.

Since the hydrogenation rates observed with benzonaphthothiophene are about three orders of magnitude greater than those observed with dibenzothiophene (Houalla et al. 1978), we conclude that there is extensive flat adsorption of benzonaphthothiophene and related compounds, implying bonding of the molecules with the catalyst surface through the π-electrons of the benzenoid rings. The importance of this kind of bonding of polycyclic aromatic compounds has been suggested earlier (e.g., Houalla et al. 1978, Singhal et al. 1978, Kwart et al. 1980).

## ACKNOWLEDGMENT

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# A Hyperboloidal Constricted Tube Model of Porous Media

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In recent years, numerous publications on flow of fluids through porous media have emphasized the need for geometric models to describe and analyze transport processes in the pores of the media. A few models, both old and new, are indeed available for this purpose, although the particular choice usually depends on the specific application under consideration. The highly simplified capillaric models serve only a limited purpose, as the curvature of the actual pores may be critical in most applications. The conceptually simple, but quite versatile, cell models (such as the sphere-in-cell model of Happel) have been used extensively in the study of heat and mass transfer in packed beds and lately have been shown to be highly successful in predicting deposition (of particles from suspensions) in porous structures (Rajagopalan and Tien 1976, 1979), but they do not account for the converging-diverging nature of the pores.

In 1973, Payatakes, Tien, and Turian proposed a periodically constricted tube model (PCT) based on Petersen's (1958) preliminary suggestion to account for the effect of neighboring grains and the converging-diverging nature of the flow channels. This PCT model has been used for studying deposition of particles in deep bed filtration (for instance, Payatakes, Tien, and Turian 1973, 1974, and Rajagopalan and Tien 1979). Another PCT model, with sinusoidal walls, has been introduced since then by Fedkiw and Newman (1977) for studying mass transfer at high Peclet numbers, and other variations have also been examined (Azzam and Dullien 1977).

These models are potentially quite useful, but their use is severely restricted by the difficulty in obtaining a *closed-form* solution to the corresponding hydrodynamic problem. The solution of the Navier-Stokes equation in these cases is difficult and requires numerical methods even for the creeping flow case. Certain applications, such as trajectory calculations in deposition studies, require the velocity fields for statistically dissimilar tubes. This implies that the above problem has to be solved (numerically) for numerous constricted tubes. Although a collocation solution to this problem, for one particular choice of tube geometry, is now available (Neira and Payatakes 1978), collocation expansion coefficients are still needed for arbitrary geometries of the constricted tubes. The above considerations make it clear that a simple, but effective, model with a closed-form expression for the stream function is highly desirable.

The purpose of this note it to present such a model. The model proposed here retains the converging-diverging character of the pore, but does not consider the pores (and hence the flow through them) to be periodic, since in many applications periodicity is not required. Geometric models of porous media have been used frequently to describe and predict the average macroscopic response of the media to the processes that occur within them (including, for example, the pressure drop, mass or heat transfer rates, and residence times). We found that the new model predicts the macroscopic parameters of the flow with the same degree of accuracy as obtained through PCT models. Besides, one is not restricted to a choice of geometrically similar constricted tubes in the case of the present model (in contrast to the PCT models). The new model has three arbitrary geometric parameters, as the previous ones, but one may consider a collection of constricted tubes of any combination of arbitrary geometric parameters, and the flow field and the pressure drop in all of them can be readily obtained as functions of these parameters.

## MODEL FORMULATION

We shall consider a packed bed to be composed of statistically identical unit bed elements (UBE) each of which in turn consists of an array of constricted tubes, as originally proposed by Payatakes et al. (1973). The walls of these tubes are generated by a one-sheeted hyperboloid of revolution about the axis of symmetry. Each tube, hereafter called Hyperboloidal Constricted Tube (HCT), is characterized by the following three geometric parameters: the length, $l$, the throat diameter, $d_t$, and the entrance (or exit) diameter, $d_e$. These parameters can be obtained by the same technique used to calculate the PCT model parameters.

A sketch of a typical hyperboloidal constricted tube is presented in Figure 1. The appropriate coordinate system in this case is the set of oblate spheroidal coordinates ($\xi$, $\eta$, $\phi$) with the origin at the center of the tube.[1] Figure 1 also shows the corresponding circular cylindrical coordinates ($r$,$z$,$\phi$). The rela-

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