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Kinetic Model for Methanol Conversion to Olefins

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This paper deals with a phenomenological model for methanol conversion to olefins. A system of linear independent reactions is built from the global reaction of methanol transformation. The mechanism of reaction, a development based on carbenoid intermediates of the above set of chemical reactions, has 27 reactions and 18 molecular species. The kinetic parameters identified using nonlinear optimization techniques, and the model predictions, agree satisfactorily with experimental data and data available in the literature.

Introduction

The catalytic conversion of methanol (MeOH) to hydrocarbons, mainly gasoline, has been intensively investigated in recent years, both economically and scientifically (Chang and Silvestri, 1977; Voltz and Wise, 1978; Chen and Reagan, 1979; Chang et al., 1979; Harney and Mills, 1980). It is known (Lin and Anthony, 1977; Voltz and Wise, 1978) that changes in the catalyst composition and structure may favor the appearance of olefins and lower the ratio of paraffins and other hydrocarbons.

Both routes for converting methanol into paraffins or olefins have in common the first steps of the reaction mechanism and subsequently specific features. To explain the process of conversion to gasoline several mechanisms were proposed, involving either carbenium ions (Derouane et al., 1978) or oxonium ions (van den Berg et al., 1980). A mechanism based on carbenoid species (Chang and Silvestri, 1977), having only four products as kinetic species, namely oxygenated compounds, olefins, paraffins, and aromatics, was recently developed (Chang, 1980). Anthony and Singh (1980) listed a set of global reactions which may occur and, according to their selectivities, distinguished the primary and secondary formed compounds. A global kinetic equation with three parameters for methanol consumption only is presented by Anthony et al. (1981).

The present study deals with the derivation of a phenomenological kinetic model describing the reaction path for MeOH conversion to olefins.

Experimental Section

The experiments have been carried out in a stainless steel tube reactor (14 mm i.d. and 750 mm length); a heating/cooling system maintained isothermicity along its height. The reactor contains 60 cm³ of catalyst. The

Table I. The Stoichiometric Matrix A

no.	molecular species	C	H	O
1.	H ₂	0	2	0
2.	CO	1	0	1
3.	CO ₂	1	0	2
4.	CH ₄	1	4	0
5.	C ₂ H ₆	2	6	0
6.	C ₂ H ₄	2	4	0
7.	C ₃ H ₈	3	8	0
8.	C ₃ H ₆	3	6	0
9.	C ₄ H ₁₀	4	10	0
10.	C ₄ H ₈	4	8	0
11.	C ₅ H ₁₂	5	12	0
12.	C ₅ H ₁₀	5	10	0
13.	C	1	0	0
14.	CH ₃ OH	1	4	1
15.	CH ₃ OCH ₃	2	6	1
16.	H ₂ O	0	2	1

MeOH was p.a. grade. Liquid MeOH, fed with a dosimetric pump, was vaporized in an inert material-filled preheating zone.

After cooling, the reaction products were separated into two fractions: the volatile fraction (H₂, dimethyl ether (DME), and C₁-C₆ hydrocarbons) and the liquid one. The liquid fraction separated into two phases: hydrocarbons with more than six carbon atoms and the aqueous phase (water, MeOH, and DME). All fractions have been subjected to vapor phase chromatographic analysis (Pop et al., 1979b).

The catalyst (Pop et al., 1979a) is a bifunctional synthetic modified mordenite zeolite containing divalent ions and having an SiO₂/Al₂O₃ ratio higher than 20. It has been used as extruded cylinders with 1.5 mm diameter and 3 mm length. The experiments have been run under atmospheric pressure at 370 °C reaction temperature.

Table II. The Set of Linear Independent Reactions

no.	reaction
1.	$2\text{CH}_3\text{OH} = \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$
2.	$2\text{CH}_3\text{OH} = \text{C}_2\text{H}_4 + \text{H}_2\text{O}$
3.	$5\text{C}_2\text{H}_4 = 2\text{C}_5\text{H}_{10}$
4.	$2\text{C}_2\text{H}_4 = \text{C}_4\text{H}_8$
5.	$3\text{C}_2\text{H}_4 = 2\text{C}_3\text{H}_6$
6.	$\text{C}_2\text{H}_4 = \text{CH}_4 + \text{C}$
7.	$2\text{C}_2\text{H}_4 + \text{CH}_4 = \text{C}_5\text{H}_{12}$
8.	$3\text{C}_2\text{H}_4 + 2\text{CH}_4 = 2\text{C}_4\text{H}_{10}$
9.	$\text{C}_2\text{H}_4 + \text{CH}_4 = \text{C}_3\text{H}_8$
10.	$\text{C}_2\text{H}_4 + 2\text{CH}_3\text{OH} = 3\text{CH}_4 + \text{CO}_2$
11.	$\text{C}_2\text{H}_4 + \text{CH}_3\text{OH} = 2\text{CH}_4 + \text{CO}$
12.	$2\text{CH}_4 = \text{C}_2\text{H}_6 + \text{H}_2$
13.	$\text{C}_2\text{H}_4 + \text{H}_2 = \text{C}_2\text{H}_6$

Assesment of a Model

In order to develop a kinetic model our approach was as follows: (i) a stoichiometric matrix proceeds directly from the components found in the experimental results; (ii) a set of linear independent reactions is chosen; (iii) reactions are deleted, supplemented, and supported through mechanistic arguments found in the literature which are in accordance with the experimental observations; (iv) a set of kinetic parameters is fitted to the system of reactions in its final form.

The Set of Linear Independent Reactions. Starting from the global reaction of conversion of methanol into olefins, we have constructed the stoichiometric matrix A , see Table I, whose elements, a_{ij} , are the number of atoms of species i in the molecules of species j . From the chemical reactions we may write

$$\sum_{j=1}^n \alpha_{ij} a_{ij} = 0 \quad (i = 1, 2, \dots) \quad (1)$$

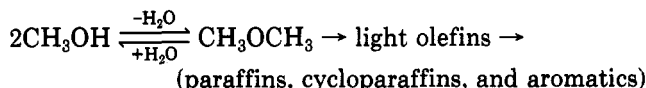
where α_{ij} is the coefficient of the j th molecular species in the i th reaction and n is the number of molecular species taken into account. The number of linear independent reactions is equal to the difference between the number of molecular species and the rank of the stoichiometric matrix A (Aris and Mah, 1963). In our case $n = 16$ and rank of A is 3, hence the number of linear independent equations is 13, whose coefficients of the molecular species are solutions of the following algebraic system in x_j ($j = 1, 2, \dots, n$)

$$\sum_{j=1}^n a_{ij} x_j = 0 \quad (i = 1, 2, \dots) \quad (2)$$

The homogeneous system (2), with 13 linear independent solutions in X , defines the set of linear independent reactions, see Table II. The linear independent reactions may be viewed as global reactions. The reaction mechanism is more complex, owing to the intermediate species through which it takes place and the parallel reactions which cannot be included in a set of linear independent reactions; as a development of the set of linear independent reactions, the reaction mechanism includes more equations, which are no longer linearly independent. Although it may be cumbersome, the mechanism of reaction describes not only the final composition, as in the case of the system of linear independent reactions, but also the kinetic path of the whole system (Aris, 1969).

Reaction Mechanism. The following reaction mechanism, a result of the set of linear independent reactions, is based on literature data and on our own experimental data. Owing to the lack of direct proofs, the present equations were proposed following the analysis of a large number of possible chemical reactions. The reaction path for the conversion of methanol to hydrocarbons has been shown to involve a sequence of steps which can be sum-

marized as follows (Chang and Silvestri, 1977; Salvador and Kladnig, 1977; Anderson et al., 1979; Chen and Reagan, 1979; Chang, 1980)

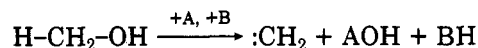


The catalyst, with both acidic and basic centers, is a synthetic zeolite with a small crystal density, which is a measure of the number, dimension, and stability of the pores (Derouane et al., 1978). Such a material is stable at high temperatures, even in the presence of steam, enabling the elimination of carbonaceous residues which may be formed during its operation as catalyst. The methanol conversion at 370 °C occurs in two major steps, i.e., the conversion to ether and the formation of hydrocarbons (Chang and Silvestri, 1977; Derouane et al., 1978; Anderson et al., 1979).

The Etherification Reaction. The dehydration of methanol occurs even at low temperatures (150–200 °C). The formation of dimethyl ether (DME) is reversible and fast enough to reach equilibrium immediately (Chang and Silvestri, 1977; Chen and Reagan, 1979; Fleckenstein et al., 1980; Chang, 1980). In a primary step the catalyst surface is completely methoxylated, so that each surface -OH group is replaced by a stable -OCH₃ group. Afterward, these -OCH₃ groups should be able to react with the methanol molecules, which are filling in the structural cavities of the catalyst (Salvador and Kladnig, 1977).

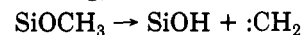
The Formation of Hydrocarbons. The formation of hydrocarbons from methanol-DME is the limiting step of the process (Chen and Reagan, 1979). Derouane et al. (1978) proposed a mechanism based on carbenium ions, which was considered improbable by Anderson et al. (1979) because in their experiments ethene, which in the above case has a major role, was relatively inert. To solve the question of the mechanism of the first C-C bond formation in ethene, a trialkyloxonium ion intermediate was proposed (van den Berg et al., 1980). The formation of CH₃-O-C⁺H₂ from DME is possible, but experiments do not suggest that this species is involved, the generation of a carbene being more probable (Anderson et al., 1979).

At high temperatures (more than 240 °C) reactions take place with formation of a carbene (Salvador and Kladnig, 1977). A separation mechanism, due to Swabb and Gates (1972), by coaction of acidic and basic centers



was rejected by Salvador and Kladnig (1977).

The carbenoid species may be formed by decomposition of the methoxylated surface due to the high temperature (Salvador and Kladnig, 1977)



where it is not necessarily meant to imply the existence of a free carbene (Chang, 1981). The strong electrostatic field of the catalyst (Derouane et al., 1978) in the zeolite cages favors the carbene formation as was pointed out by Chang and Silvestri (1977). The decomposition of methanol-DME into carbene was found to be first order with respect to the oxygenated compounds (Chang, 1980).

The Carbene Reactions. The carbene is a "hot" radical with excess energy; in any particular system many possible reactions of carbene occur with closely similar probabilities, the rates being insensitive to the small differences in activation energy (Kirmse, 1964; Hine, 1964). The attack of carbene on methanol-DME is an insertion into a C-H bond, forming higher alcohols or ethers (Frey and Voisey, 1968), which, once formed, are rapidly converted into

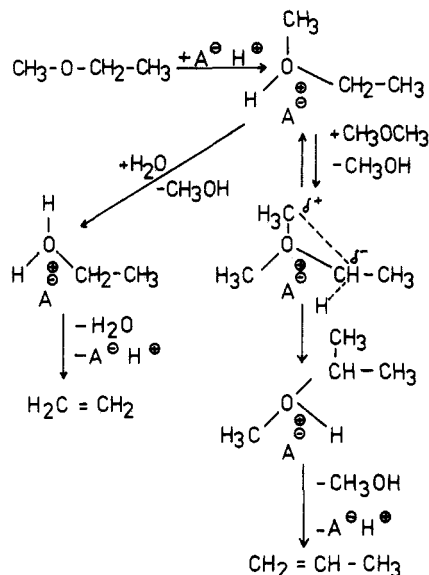
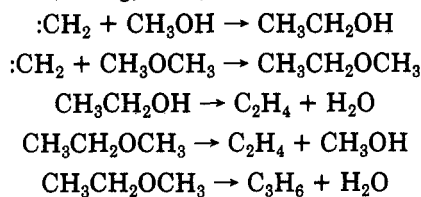


Figure 1. The methyl ethyl ether conversion to light olefins.

corresponding olefins. This is suggested by the failure to detect more than trace quantities of higher oxygenates in the products (Chang, 1980).



The formation of ethene and propene as primarily formed olefins in the conversion of methanol to olefins may be explained, according to van den Berg et al. (1980) as indicated in Figure 1. Chang et al. (1979) reported an increasing selectivity for propene upon lowering the pressure of methanol in experiments on methanol conversion. Since methanol is first converted to DME and water, because of the hydrophobic character of the zeolite (van den Berg et al., 1980), the concentration of water in the pores will be lowered to a greater extent than the concentration of DME. But the DME conversion to propene, in opposition with the DME conversion to ethene, does not imply water; therefore the propene selectivity should increase. On the other hand, if water is introduced into the feed, the ethene selectivity should increase, as reported by Givens et al. (1978).

The attack of carbene on ethene gives rise to two products (Kirmse, 1964; Hine, 1962): propene by an insertion into a C-H bond, and cyclopropane by addition to the double bond. The cyclopropane has all the energy carried by the "hot" diradical and the ethene; this is considerably more than the activation energy for the isomerization of cyclopropane to propene (Kirmse, 1964). If the reactions were carried out in the liquid phase, all the cyclopropane molecules would become deexcited and hence stabilized, but in the gas phase the proportion of stabilized molecules will depend on the lifetime of the excited cyclopropane compared with the time taken for the molecule to undergo a collision; this latter time will be pressure dependent (Kirmse, 1964); see Figure 2. Although the relative rate of addition to the double bond compared with insertion into a C-H bond is large (22.7:1), owing to the high rate of isomerization of cyclopropane, only the propene formation is taken into account (Kirmse, 1964).

The attack of carbene on propene and butene is described in the same terms (Kirmse, 1964; Hine, 1964).

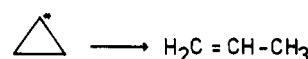
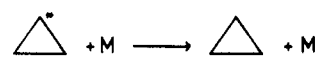
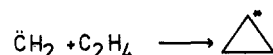
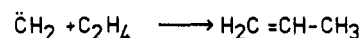


Figure 2. The carbene attack on ethene.

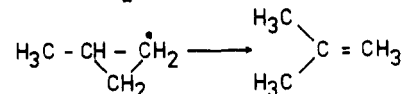
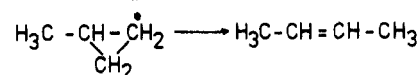
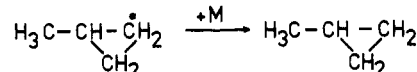
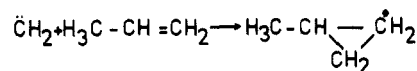
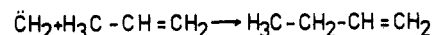
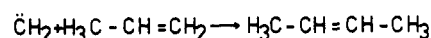
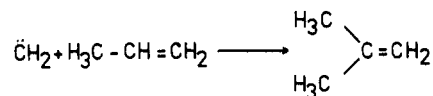


Figure 3. The carbene attack on propene.

Carbene inserts considerably more rapidly into tertiary C-H bonds than with secondary C-H bonds, and more rapidly with the latter C-H bonds than into primary C-H bonds. The branched isomers will be prevailing (Kirmse, 1964; Hine, 1962; Derouane et al., 1978); see Figure 3.

The attack of carbene on hydrogen is an insertion into an H-H bond, more rapid than into a C-H bond, giving rise to methane (Kirmse, 1964; Hine, 1962). Another reaction producing methane is the demethanization of paraffins. The carbene dimerization is negligible (Chang and Silvestri, 1977; Kistiakovsky and Sauer, 1956).

The Conversion of Olefins into Paraffins. The conversion of olefins into paraffins is first order with respect to olefins (Chang, 1980). The catalyst, with its cages and channels, appears as a solid, crystalline structure in which high electrostatic gradients prevail, favoring and stabilizing the carbenium ions (Derouane et al., 1978).

The proposed mechanism involves as a slow stage the appearance of the protonated species, due to the acid character of the catalyst (Derouane et al., 1978; Anderson et al., 1979; Salvador and Kladnig, 1977). The attack of this intermediate on the olefins (Derouane et al., 1978; Chen and Reagan, 1979) is rapid and the whole process will have first-order kinetics. The olefins reactivity depends on the structure, ethene being the least active one (Anderson et al., 1979). The transfer of proton in the conversion of olefins into paraffins is preferentially from higher olefins to lower olefins (Anderson et al., 1979)

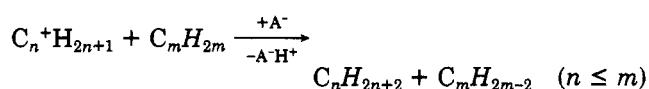
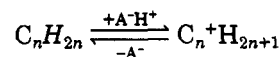


Table III. The Kinetic Model

no.	reaction	reaction rate	kinetic parameters
1	$2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$	$v_r = k_1(\text{CH}_3\text{OH})^2$ $v_r' = k_{-1}(\text{CH}_3\text{OCH}_3)(\text{H}_2\text{O})$	$K = 2.71$
2	$\text{CH}_3\text{OCH}_3 \rightarrow 2:\text{CH}_2 + \text{H}_2\text{O}$	$v_r = k_2(\text{CH}_3\text{OCH}_3)$	$k_2 = 6.05 \text{ 1/s}$
3	$:\text{CH}_2 + \text{CH}_3\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$	$v_r = k_3(:\text{CH}_2)(\text{CH}_3\text{OH})$	$k_3 = 3.2 \times 10^4 \text{ L/mol s}$
4	$:\text{CH}_2 + \text{CH}_3\text{OCH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_3\text{OH}$	$v_r = k_4(:\text{CH}_2)(\text{CH}_3\text{OCH}_3)$	$k_4 = 2.89 \times 10^4 \text{ L/mol s}$
5	$:\text{CH}_2 + \text{CH}_3\text{OCH}_3 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O}$	$v_r = k_5(:\text{CH}_2)(\text{CH}_3\text{OCH}_3)$	$k_5 = 1.2 \times 10^4 \text{ L/mol s}$
6	$:\text{CH}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_6$	$v_r = k_6(:\text{CH}_2)(\text{C}_2\text{H}_4)$	$k_6 = 5.05 \times 10^4 \text{ L/mol s}$
7	$:\text{CH}_2 + \text{C}_3\text{H}_6 \rightarrow \text{C}_4\text{H}_8$	$v_r = k_7(:\text{CH}_2)(\text{C}_3\text{H}_6)$	$k_7 = 5.05 \times 10^4 \text{ L/mol s}$
8	$:\text{CH}_2 + \text{C}_4\text{H}_8 \rightarrow \text{C}_5\text{H}_{10}$	$v_r = k_8(:\text{CH}_2)(\text{C}_4\text{H}_8)$	$k_8 = 1.2 \times 10^4 \text{ L/mol s}$
9	$:\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_4$	$v_r = k_9(:\text{CH}_2)(\text{H}_2)$	$k_9 = 2.36 \times 10^5 \text{ L/mol s}$
10	$\text{C}_2\text{H}_4 \xrightleftharpoons[-\text{A}^-]{+\text{A}^-\text{H}^+} \text{C}_2^+\text{H}_5$	$v_r = k_{10}(\text{C}_2\text{H}_4)$ $v_r' = k_{-10}(\text{C}_2^+\text{H}_5)$	$k_{10} = 0.111 \text{ 1/s}$ $K = 0.0302$
11	$\text{C}_3\text{H}_6 \xrightleftharpoons[-\text{A}^-]{+\text{A}^-\text{H}^+} \text{C}_3^+\text{H}_7$	$v_r = k_{11}(\text{C}_3\text{H}_6)$ $v_r' = k_{-11}(\text{C}_3^+\text{H}_7)$	$k_{11} = 0.388 \text{ 1/s}$ $K = 0.105$
12	$\text{C}_4\text{H}_8 \xrightleftharpoons[-\text{A}^-]{+\text{A}^-\text{H}^+} \text{C}_4^+\text{H}_9$	$v_r = k_{12}(\text{C}_4\text{H}_8)$ $v_r' = k_{-12}(\text{C}_4^+\text{H}_9)$	$k_{12} = 0.813 \text{ 1/s}$ $K = 0.221$
13	$\text{C}_5\text{H}_{10} \xrightleftharpoons[-\text{A}^-]{+\text{A}^-\text{H}^+} \text{C}_5^+\text{H}_{11}$	$v_r = k_{13}(\text{C}_5\text{H}_{10})$ $v_r' = k_{-13}(\text{C}_5^+\text{H}_{11})$	$k_{13} = 0.813 \text{ 1/s}$ $K = 0.221$
14	$\text{C}_n^+\text{H}_{2n+1} + \text{C}_m\text{H}_{2m} \xrightleftharpoons[-\text{A}^-\text{H}^+]{+\text{A}^-} \text{C}_n\text{H}_{2n+2} + \text{C}_m\text{H}_{2m-2}$	$v_r = k_{14}(\text{C}_n^+\text{H}_{2n+1})(\text{C}_m\text{H}_{2m})$	$k_{14} = 80.0 \text{ L/mol s}$
15	$\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$	$v_r = k_{15}(\text{C}_2\text{H}_4)(\text{H}_2)$	$k_{15} = 8.3 \times 10^{-5} \text{ L/mol s}$
16	$\text{C}_3\text{H}_6 + \text{H}_2 \rightarrow \text{C}_3\text{H}_8$	$v_r = k_{16}(\text{C}_3\text{H}_6)(\text{H}_2)$	$k_{16} = 5.0 \times 10^{-4} \text{ L/mol s}$
17	$\text{C}_4\text{H}_8 + \text{H}_2 \rightarrow \text{C}_4\text{H}_{10}$	$v_r = k_{17}(\text{C}_4\text{H}_8)(\text{H}_2)$	$k_{17} = 5.0 \times 10^{-4} \text{ L/mol s}$
18	$\text{C}_5\text{H}_{10} + \text{H}_2 \rightarrow \text{C}_5\text{H}_{12}$	$v_r = k_{18}(\text{C}_5\text{H}_{10})(\text{H}_2)$	$k_{18} = 5.0 \times 10^{-4} \text{ L/mol s}$
19	$\text{C}_3\text{H}_8 \rightarrow \text{C}_2\text{H}_4 + \text{CH}_4$	$v_r = k_{19}(\text{C}_3\text{H}_8)$	$k_{19} = 0.495 \text{ 1/s}$
20	$\text{C}_4\text{H}_{10} \rightarrow \text{C}_3\text{H}_6 + \text{CH}_4$	$v_r = k_{20}(\text{C}_4\text{H}_{10})$	$k_{20} = 0.813 \text{ 1/s}$
21	$\text{C}_5\text{H}_{12} \rightarrow \text{C}_4\text{H}_8 + \text{CH}_4$	$v_r = k_{21}(\text{C}_5\text{H}_{12})$	$k_{21} = 2.23 \text{ 1/s}$
22	$\text{CH}_3\text{OH} \rightleftharpoons \text{CO} + 2\text{H}_2$	$v_r = k_{22}(\text{CH}_3\text{OH})$ $v_r' = k_{-22}(\text{CO})(\text{H}_2)^2$	$K_{22} = 0.495 \text{ 1/s}$ $K = 7.0 \times 10^4 (\text{mol/L})^2$
23	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	$v_r = k_{23}(\text{CO})(\text{H}_2\text{O})$	$k_{23} = 1.32 \times 10^{-3} \text{ L/mol s}$
24	$\text{C}_2\text{H}_4 \rightarrow \text{CH}_4 + \text{C}$	$v_r = k_{24}(\text{C}_2\text{H}_4)$	$k_{24} = 0.111 \text{ 1/s}$
25	$\text{C}_2\text{H}_6 + \text{H}_2 \rightarrow 2\text{CH}_4$	$v_r = k_{25}(\text{C}_2\text{H}_6)(\text{H}_2)$	$k_{25} = 2.67 \times 10^{-3} \text{ L/mol s}$
26	$\text{C}_4\text{H}_6 + \text{H}_2 \rightarrow \text{C}_4\text{H}_8$	$v_r = k_{26}(\text{C}_4\text{H}_6)(\text{H}_2)$	$k_{26} = 1.32 \times 10^{-3} \text{ L/mol s}$
27	$\text{C}_5\text{H}_8 + \text{H}_2 \rightarrow \text{C}_5\text{H}_{10}$	$v_r = k_{27}(\text{C}_5\text{H}_8)(\text{H}_2)$	$k_{27} = 1.32 \times 10^{-3} \text{ L/mol s}$

Fleckenstein et al. (1980) detected paraffin formation only when the catalyst had an acidic character, a fact which supports the above idea.

Presence of Carbon Oxides. The methanol decomposition into carbon monoxide and hydrogen, taking place with growth of volume, is favored at low pressure. The attack of carbene on hydrogen and the small contact time do not allow the formation of paraffins from carbon monoxide and hydrogen. The decomposition of carbon monoxide into carbon dioxide and carbon is taken to be slower than the ethene decomposition into carbon and methane, and therefore is neglected. Only the reaction of carbon monoxide with steam, giving rise to carbon dioxide, is taken into account.

Secondary Reactions. The hydrogenolysis of paraffins or the molecular hydrogenation of olefins, with second-order kinetics (Hinshelwood, 1955) are of secondary importance (Weisz, 1962). The thermal decomposition of DME is neglected because of its high activation energy and because the equilibrium constant is equal to unity at 800 K (Hinshelwood, 1955; Senderens, 1912).

As can be seen, the major incertitude concerning the mechanism of reaction lies in the emergence of the first C-C bond. It is most probable that behind the two main assumptions, involving carbene or ions, a more complex reality is hidden. The final step of such a process could be either a concerted insertion into a C-H bond or addition to a double bond (Chang and Silvestri, 1977). For the time being one has only to adhere to the statement made by Chang (1981): "the primary mechanism of C-C bond

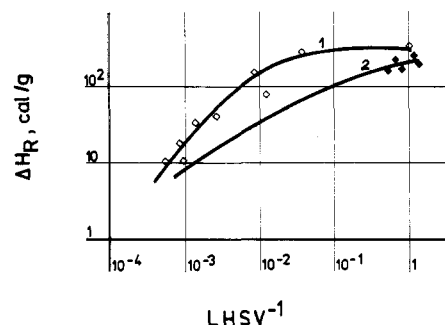


Figure 4. The heat of reaction: (1) Chang and Silvestri (1977); (2) this paper; (○) Chang and Silvestri (1977), experimental values; (●) this paper, experimental values.

formation from methanol remains an open question".

Results and Discussion

The results of the analyses are shown in Table V which is available as supplementary material (see the paragraph at the end of the article regarding availability). The coke and unidentified species representing about 5% in weight are omitted.

The reactions of the proposed mechanism and their rate expressions are listed in Table III. The kinetic parameters of the nonlinear system were estimated through a Marquardt search routine (Marquardt, 1963), modified by Fletcher (1971) and adapted by us for an IRIS computer. The objective function, computed as the weighted sum of squares of deviations from the five sets of data presented

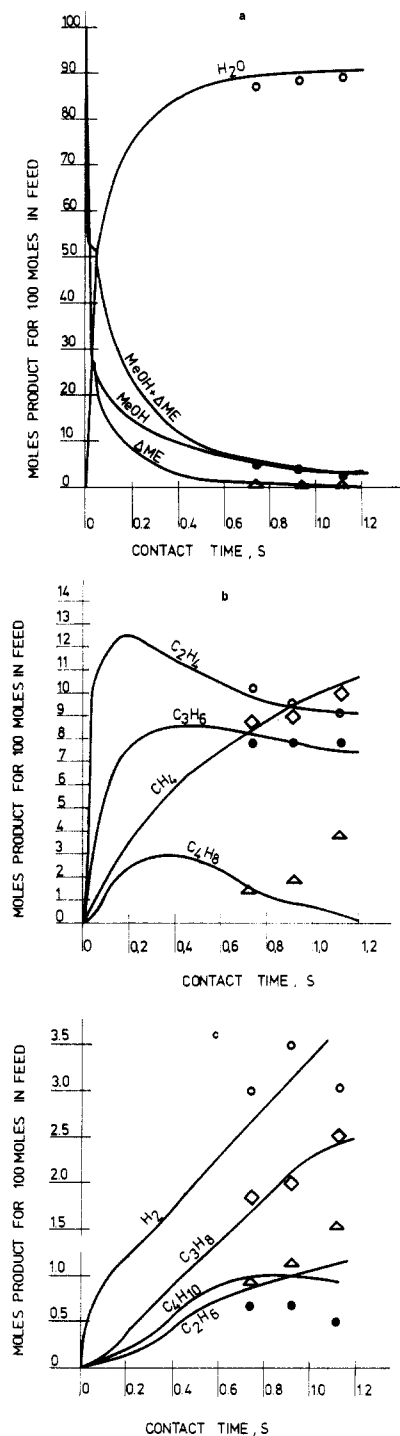


Figure 5. The major products distribution for the pure methanol conversion: (a) (●) MeOH; (Δ) DME; (○) H₂O, experimental values; (b) (◇) CH₄; (○) C₂H₄; (●) C₃H₆; (Δ) C₄H₈, experimental values; (c) (○) H₂; (●) C₂H₆; (◇) C₃H₈; (Δ) C₄H₁₀, experimental values.

in Table V, provides a hypersurface with many local extrema. The few available literature data have been used by us to produce different starting points, because our problem is very sensitive to initial solutions; the best set of kinetic parameters found in this manner has been retained as the optimum solution. The gradient required by the algorithm has been computed numerically by a Runge-Kutta-Gear method.

An analysis of the kinetic constants is presented in Table IV. It underlines the role of the carbene generation reaction and the first-order kinetics of the olefins conversion to paraffins. We may conclude that molecular hydrogenation and hydrogenolysis are of secondary importance.

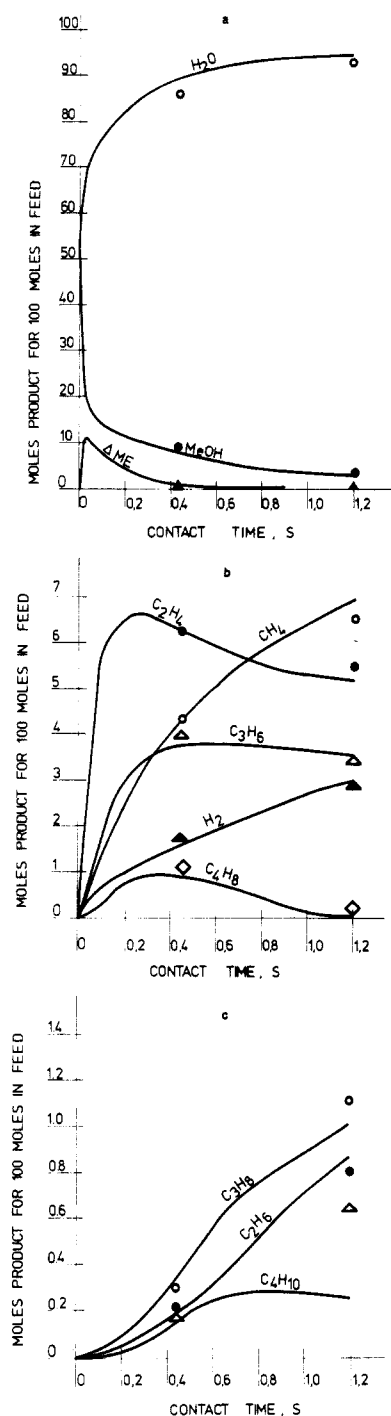


Figure 6. The major products distribution for the 50 mol % methanol-50 mol % water conversion: (a) (●) MeOH; (Δ) DME; (○) H₂O, experimental values; (b) (▲) H₂; (○) CH₄; (●) C₂H₄; (Δ) C₃H₆; (◇) C₄H₈, experimental values; (c) (●) C₂H₆; (○) C₃H₈; (Δ) C₄H₁₀, experimental values.

Chen and Reagan (1979) proposed an autocatalytic model



The first step is the slow one. In our model, the slow step is the carbene generation, with a kinetic constant of 3.01 s^{-1} (in terms of methanol) which is not too far from 1.1 s^{-1} in the above case.

The heat of reaction, which resulted from experiments and simulation, is presented in Figure 4. It is lower than that reported by Chang and Silvestri (1977) owing to the

Table IV. The Kinetic Parameters Ratios

no.	kinetic parameters ratios	C ₂	C ₃	C ₄	C ₅	global value ^a
1.	(carbene addition to C=C of olefin C _i)/ (carbene insertion into C-H of CH ₃ OH)	1.58	1.58	0.375	-	2.77
2.	(carbene addition to C=C of olefin C _i)/ (carbene insertion into C-H of CH ₃ OCH ₃)	1.24	1.24	0.294	-	
3.	(olefins conversion to paraffins)/ (carbene generation)	0.018	0.064	0.134	0.134	0.197
4.	(protonated species generation)/ (protonated species consumption)	0.0014	0.0047	0.0100	0.0100	-
5.	(olefins conversion to paraffins)/ (molecular hydrogenation)	1330.	776.	1620.	1620.	-
6.	(hydrogenolysis C ₂)/ (demethanization C ₃)	0.053	-	-	-	-
7.	(demethanization)/ (olefins conversion to paraffins)	-	1.27	1.0	2.74	-

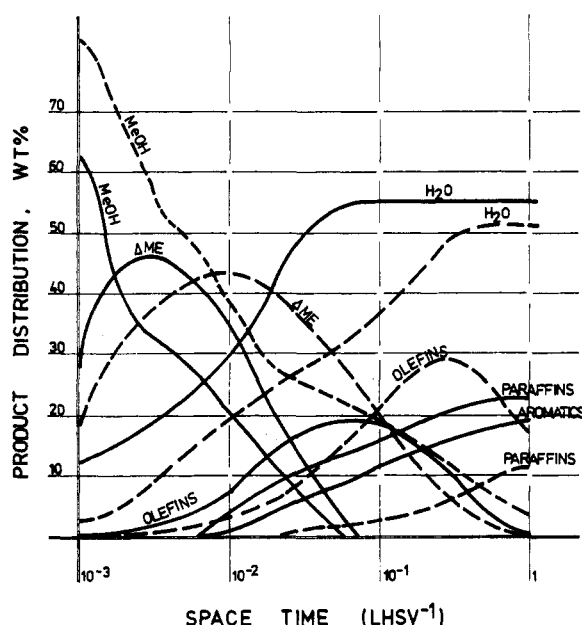
^a Chang (1980).

Figure 7. The products distribution for the pure methanol conversion: (—) Chang et al. (1979); (---) this paper.

lack of aromatics.

In Figure 5 the major products distribution is presented for the case of pure methanol, as a function of the contact time such as it is described by our own model, and it is compared with our experimental data. Varying the feed composition may change the hydrocarbons selectivity: the presence of steam quenches the Lewis acidity (Anderson et al., 1979) and the ethene selectivity is increased. In Figure 6 the major products distribution is presented as a function of the contact time when the feed is methanol with water. As a whole, our results agree quite well with those of Chang et al. (1979) and Chang and Silvestri (1977), to which comparison is made in Figures 7 and 8, where, in the second one, we restricted to the model prediction only.

The methanol curve has a first slope corresponding to the etherification reaction, and a second one is related to its conversion into hydrocarbons. The DME has a maximum corresponding to the equilibrium reached in the etherification reaction.

The olefins have a maximum, and afterward their conversion to paraffins prevails; on the other hand, the paraffins grow all the time.

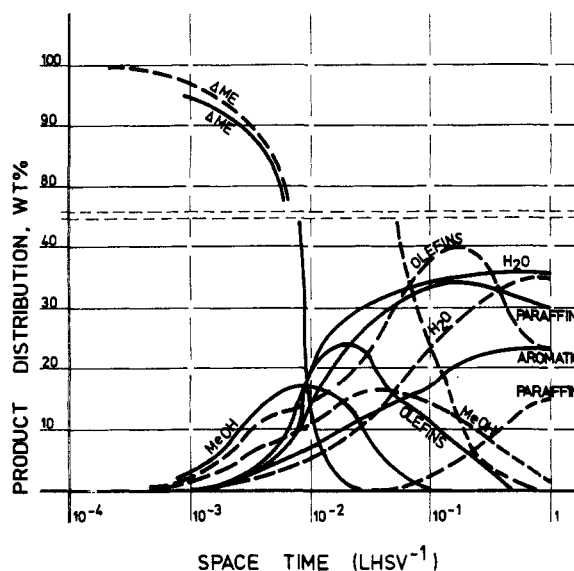


Figure 8. The products distribution for the pure ether conversion: (—) Chang and Silvestri (1977); (---) this paper.

The water is increasing rapidly due to the conversion of methanol into hydrocarbons, that is olefins firstly, and has a near constant value during the conversion of olefins into paraffins.

Comparison of the experimental results with other reported data (Chang and Silvestri, 1977; Lin and Anthony, 1977; Derouane et al., 1978; Liederman et al., 1978; Chang et al., 1978; Chang et al., 1979; Yurchak et al., 1979; Morgan et al., 1981) underlines the strong influence of the operating conditions and catalyst structure on the product distribution.

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Registry No. MeOH, 67-56-1; CH₂, 2465-56-7; DME, 115-10-6.

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Supplementary Material Available: Table V. The experimental data for conversion of methanol to olefins (2 pages). Ordering information is given on any current masthead page.

Simple Field Test Model for Underground Coal Gasification

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A simple process model was used to study the effects certain variables had on the product gas composition from a subbituminous, steeply dipping underground coal gasification field test. We found that two key model input parameters were (1) heat loss and (2) the ratio CO/CO_2 in the carbon oxidation equation. An increase in the heat loss parameter was generally accompanied by a decrease in the CO/CO_2 parameter in order to fit the field test data. The heat loss parameter increased as the field test progressed, suggesting increased rock fall or ground water influx. Very late in the field test, the only way to fit the data was by substituting a "fictional" coal having a high char/volatile ratio. We conclude that as the process module aged, the production of char (relative to volatiles) increased.

I. Introduction

Several mathematical models have been developed and used to study field test data from underground coal gasification. Gunn and Whitman (1976) developed a one-dimensional model to study the gasification of a Hanna, WY, subbituminous coal. Jennings et al. (1977) simplified the Gunn work by substituting algebraic relationships for the reaction rate expressions. Thorsness and Sherwood (1978) developed a model which includes more reactions than the Gunn model but requires more input information. We have used the Jennings model to evaluate results from a subbituminous, steeply dipping field test at Rawlins, WY. We have compared model calculations of product gas composition with the measured values. Using the model, we showed that observed changes in product gas composition could be related to changes in unmeasured, uncontrolled process variables such as heat loss. This paper presents such results.

II. Field Test Description

A schematic of the Rawlins Steeply Dipping bed is shown in Figure 1. The test was done in a forward gasification mode. The consumption of coal began near the

injection well and advanced toward the product well. Air and water were injected for most of the field test, except for a five-day period of oxygen-steam injection at the end of the test.

Neither groundwater influx, heat loss, nor reaction temperature was directly measured during the test. The absence of direct information on these variables led us to use the model to quantitatively estimate what effects they might have had.

III. Model Description

A. One-Dimensional Model. The one-dimensional model developed by Jennings is illustrated in Figure 2. Energy and material balances are performed on a control volume of unit cross section. Coal with a given proximate analysis, density, and volatile composition enters the control volume at a temperature T_{COL} . Injected oxygen, nitrogen, and steam enter at a temperature T_{INJ} . Liquid water (W_R), including both injected water and groundwater, enters at T_{COL} . Ash leaves the control volume at T_{ASH} and product gas, at T_{OUT} . Heat loss is expressed by the term " L_R ", which is defined as the quotient of heat losses divided by the heat generated by the combustion reaction of C with O_2 to produce CO and CO_2 . The model's