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DIRECT SYNTHESIS OF 2-METHYL-1-PROPANOL/METHANOL FUELS AND FEEDSTOCKS

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OBJECTIVES AND SCOPE OF WORK

The objective of this research project is to provide a technological and scientific foundation for the synthesis of 2-methyl-1-propanol/methanol fuels and basic chemicals from synthesis gas. These mixtures are excellent high octane fuels, can be blended with hydrocarbon gasoline, have high energy densities in the 2-methyl-1-propanol portion, and have synthesis stoichiometries that can be adjusted to the various H_2/CO ratios produced by different gasifiers and feedstocks.

The two principal tasks involve the following lines of research:

(i) the development and optimization of Cs/Cu/ZnO support catalysts wherein the cesium component provides a very effective basic function that steers the synthesis toward 2-methyl-1-propanol, and

(ii) the development of a kinetic reaction network that will be usable for reactor design, as well as for prediction of reaction conditions that give rise to the required 2-methyl-1-propanol/methanol composition in the reactor exit stream.

Auxiliary tasks of this research project that will utilize and build upon the data and principles derived from the two primary tasks deal with

(iii) providing mechanistic input into the kinetic modelling scheme based on experimental research using chemical

trapping of surface intermediates, isotopic studies, and insitu infrared spectroscopy,

(iv) exploratory research into novel basic components, consisting of aluminosilicates and amines, that promote branching during carbon-carbon bond formation, and

(v) concurrent characterization of the catalysts by gaseous chemisorption techniques and by utilizing the modern techniques of HR-TEM, STEM, electron and X-ray diffraction, X-ray photoelectron spectroscopy, and vibrational spectroscopies such as laser Raman microprobe spectroscopy.

SUMMARY OF PROGRESS

A five parameter kinetic reaction network has been developed for the synthesis of oxygenates from synthesis gas over a 0.4% Cs promoted Cu/ZnO catalyst. The model successfully describes the 16-compound alcohol and ester product distribution obtained over this catalyst for a range of operating conditions, and it has been used to predict the conditions required to attain specified 2-methyl-1-propanol/ methanol selectivities and yields. The most important carbon-carbon bond forming reactions of the model are insertion leading to linear alcohols and ß-addition leading to 2-methyl branched primary alcohols. Estimates of the model parameters show that ß-addition is faster than insertion, the first carbon-carbon bond forming step of the network, and this results in high yields of methanol and 2-methyl-1-propanol. The temperature dependence and apparent activation energy was determined for each of the model parameters, thus allowing the prediction of the product composition in a wide range of process conditions. Additional studies, in which ^{13}C labelled alcohols have been added to the feed gas, show that the distribution of the ^{13}C in the product alcohols and esters is consistent with the proposed reaction paths of the kinetic network.

A medium term stability test with the Cs promoted Cu/ZnO catalyst has been carried out at conditions predicted by the model to maximize the alcohol yield while maintaining a 70/30 weight ratio of methanol to higher alcohols. Deactivation of this catalyst by exposure to iron carbonyl was then investigated, and it was found that the rate of deactivation was proportional to the rate of iron deposition on this catalyst. Long term tests are being carried out for the determination of the catalyst performance in the absence of iron carbonyls.

TECHNICAL PROGRESS

A) Development of a kinetic reaction network for the oxygenate synthesis

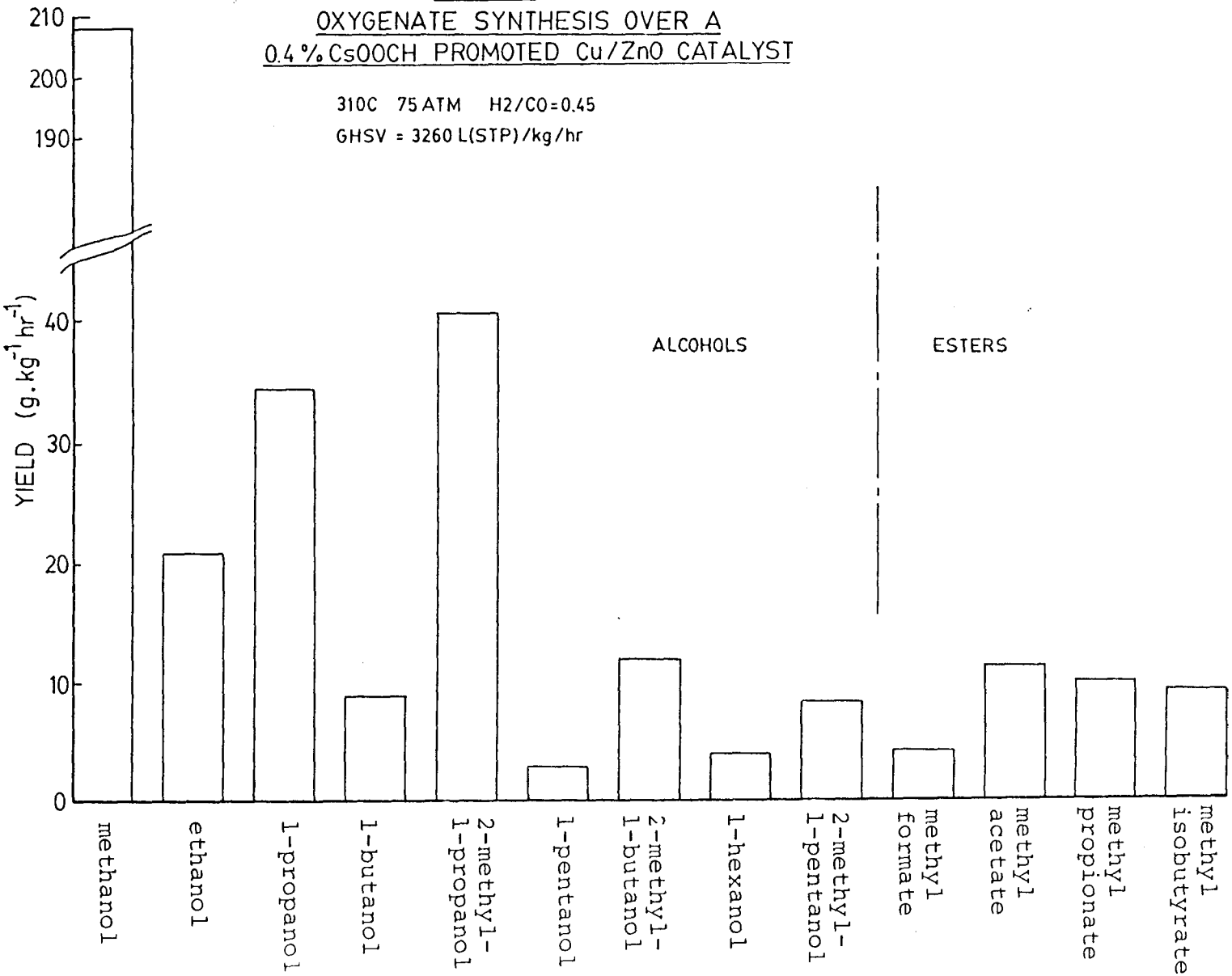
Previous work has shown that the selectivity to higher alcohols, particularly 2-methyl-1-propanol, is maximized by doping the binary Cu/ZnO catalyst with 0.4 mol% CsOOCH (*1*). Figure 1 shows the oxygenate product distribution obtained with such a catalyst at the typical higher alcohol synthesis conditions of 310°C, 75 atm, H_2/CO = 0.45 and a gas hourly space velocity (GHSV) of 3265 L(STP)/kg catalyst/hr. The product distribution is not described by the Anderson-Schulz-Flory equation applicable in the usual Fischer-Tropsch synthesis. Unique features of the distribution at these conditions include the maximum in 2-methyl-1-propanol yield, higher yields of 2-methyl branched alcohols compared to linear alcohols, a selectivity to 1-propanol greater than ethanol and significant quantities of methyl esters in the product.

Recently, a kinetic network for the alcohol synthesis over a 0.5% K_2CO_3 promoted Cu/ZnO catalyst has been proposed by Smith and Anderson (*2*), and their proposal is summarized in Figure 2. Equations that relate the alcohol distribution to the rate constants of the reaction network may be derived from the proposed model by assuming a steady-state surface concentration of the reactive intermediates. Applying the equations derived by Smith and Anderson to the data of Figure 1 results in the predicted distribution shown in Figure 3. Although the reaction network does predict the

FIGURE1

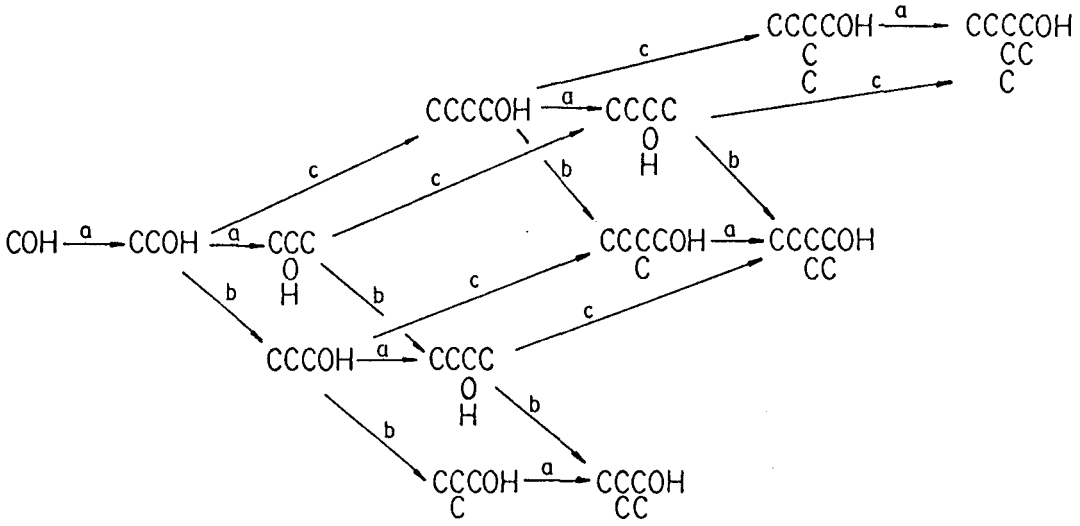
OXYGENATE SYNTHESIS OVER A
0.4 % CsOOCH PROMOTED Cu/ZnO CATALYST

310C 75 ATM H2/CO=0.45
GHSV = 3260 L(STP)/kg/hr



REACTION NETWORK FOR ALCOHOL SYNTHESIS

OVER K_2CO_3/Cu/ZnO CATALYST

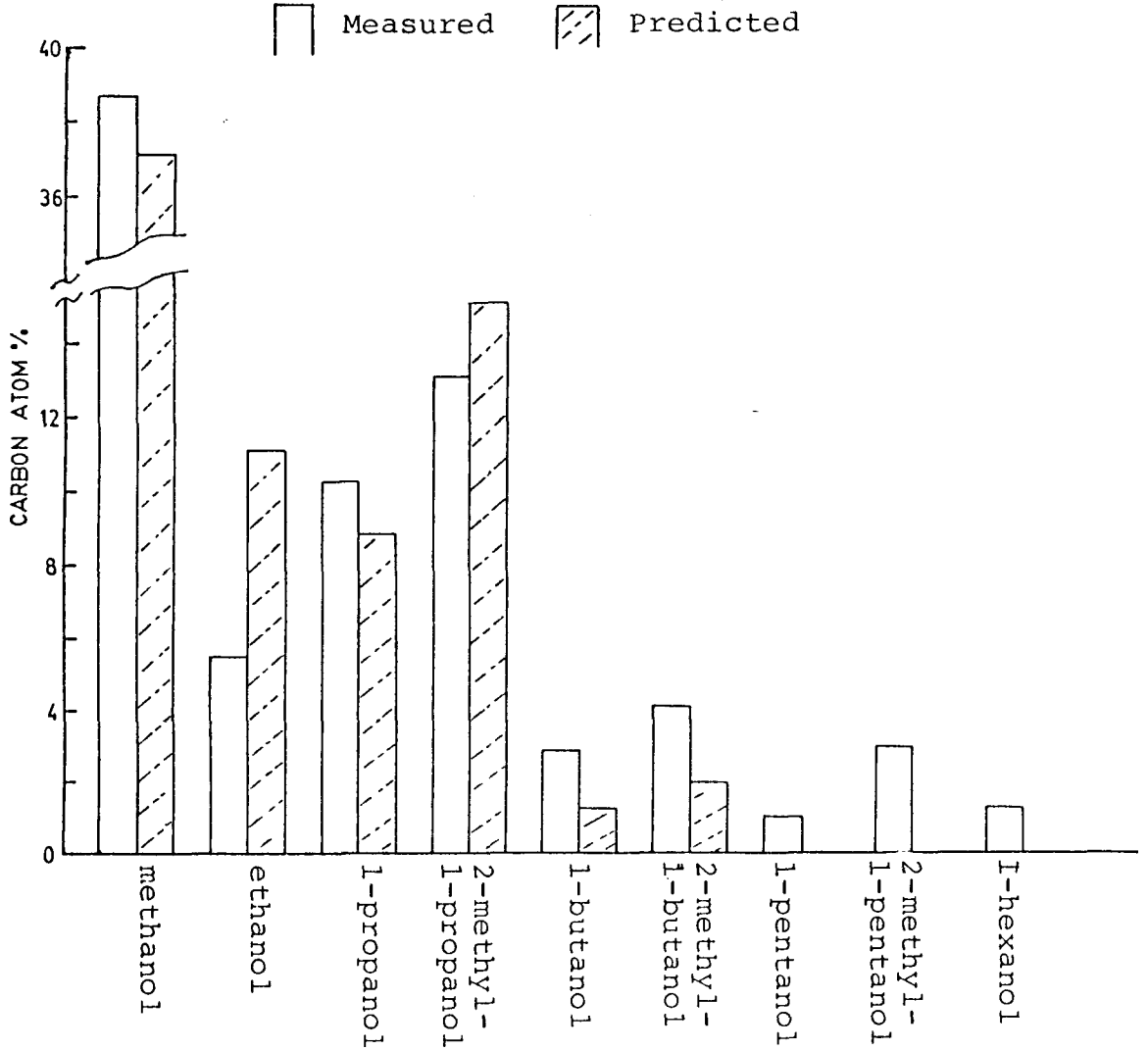


$C_3/C_2 = \beta/(1+\beta+\alpha+\gamma)$ $\quad iC_4/C_3 = \beta/(1+\alpha)$

Smith,K.J. and Anderson,R.B., J.Catal. 85 428-436 (1984)

Figure 2: Reaction network proposed by Smith and Anderson (2) for the alcohol synthesis on a K_2CO_3 promoted Cu/ZnO catalyst.

Figure 3: Smith and Anderson model applied to selectivity data at 310 C, 75atm, $H_2/CO=0.45$, and GHSV=3265 L(STP)/kg/hr, on 0.4%CsOOCH promoted Cu/ZnO catalyst.

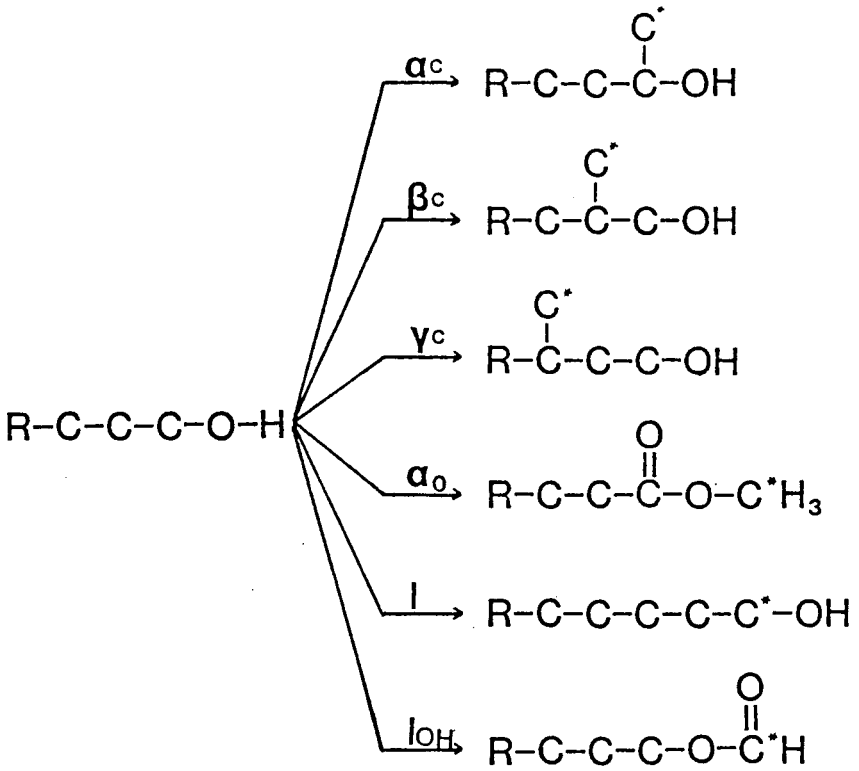


maximum in 2-methyl-1-propanol selectivity, important differences between the predicted and measured selectivities occur for ethanol and the linear alcohols greater than butanol. Furthermore, the proposal does not predict the methyl esters observed in the product.

Vedage et al. (3) have proposed alternative reaction paths for the alcohol synthesis as shown in Figure 4. The three important steps assumed to occur on Cs/Cu/ZnO catalysts are insertion leading to linear alcohols, ß-addition leading to 2-methyl branched primary alcohols and α_o-addition for methyl ester formation. Figures 5 and 6 compare the measured and predicted selectivities based on Vedage's proposal. From these figures, it is concluded that this proposal is an improvement over the proposal of Smith and Anderson because both the esters and alcohols above C_4 are predicted by this proposal.

A Five-Parameter Model

The data of Figure 5 and 6 show significant differences between the measured and predicted selectivities for some of the oxygenated products. At 270°C, the methyl ester and 1-butanol predictions are about an order of magnitude lower than the observed values. At 310°C, the predicted methyl formate selectivity is greater than the measured selectivity, while the predicted values of 1-pentanol and 2-methyl-1-butanol are significantly lower than the measured values. Furthermore, the propanol/ethanol mole ratio predicted by the Vedage et al. model



Vedage et al. ACS Symp. Ser. 279 295 (1983)

Figure 4: Possible reaction paths proposed by Vedage et al. (3) for oxygenate synthesis on Cs/Cu/ZnO catalysts.

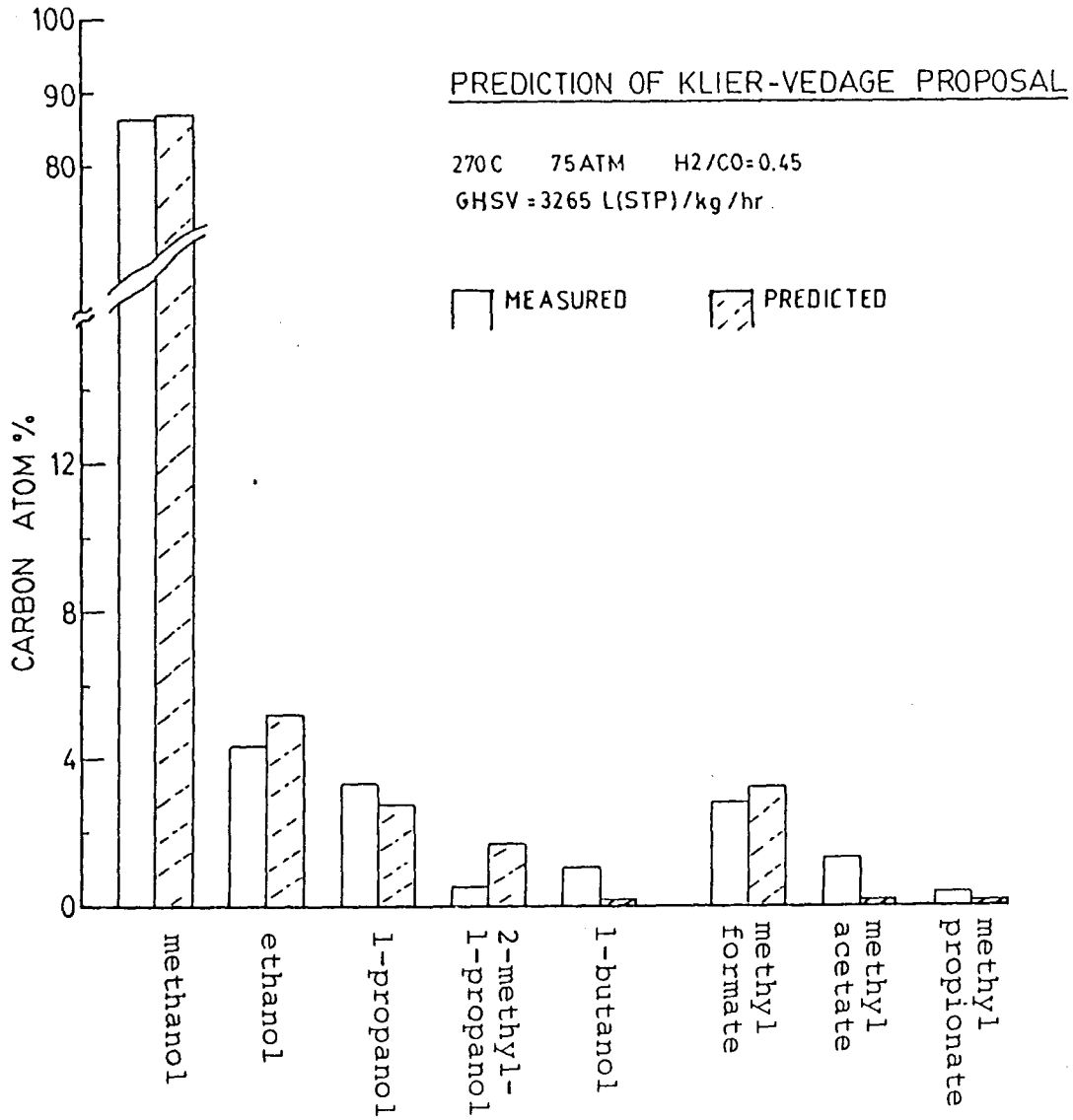


Figure 5: Proposal of Vedage et al. applied to selectivity data at 270 C, 75atm, $H_2/CO=0.45$ and GHSV=3265 L(STP)/kg/hr on 0.4% CsOOCH promoted Cu/ZnO catalyst.

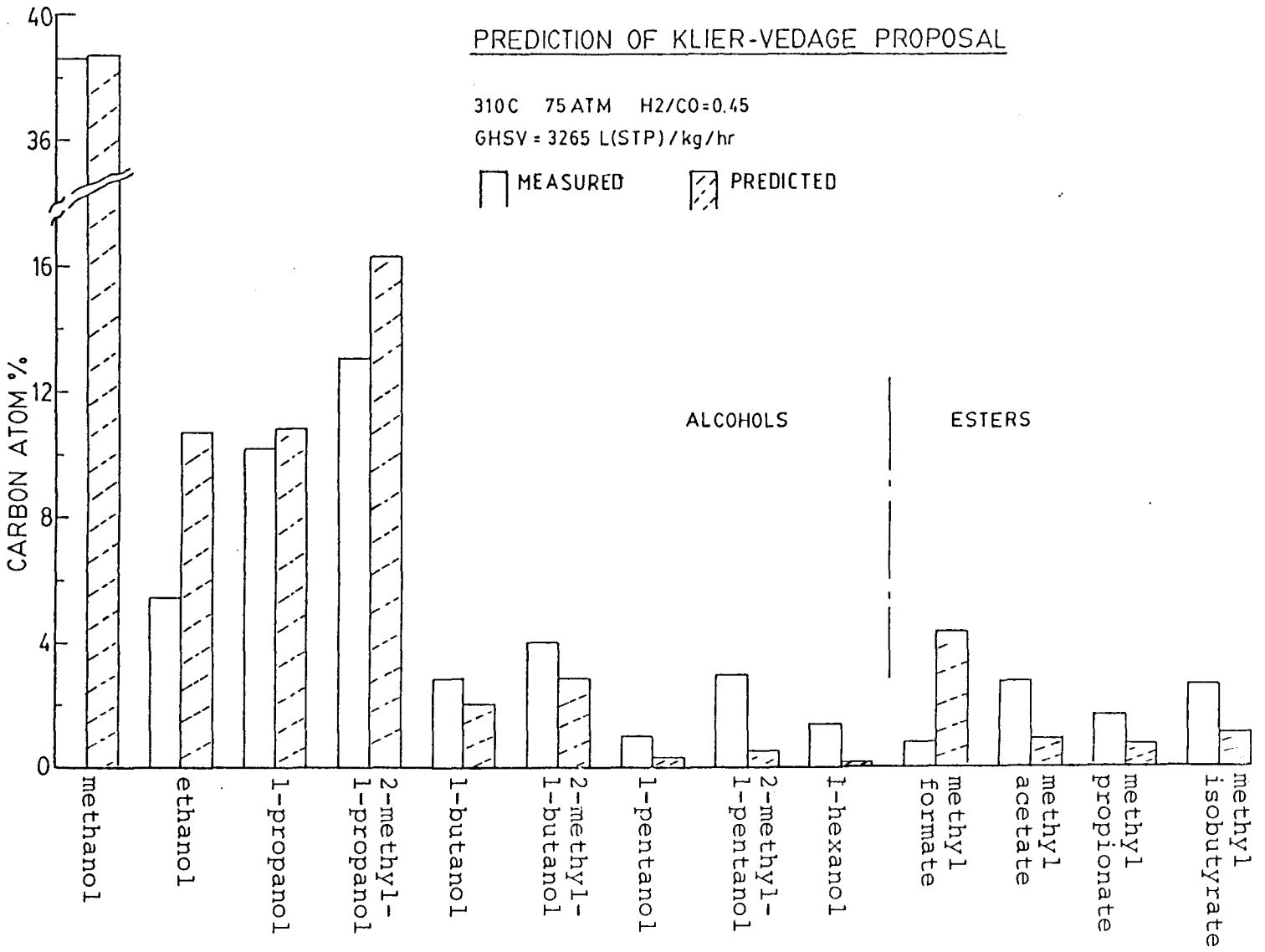


Figure 6: Proposal of Vedage et al.(3) applied to selectivity data at 310 C, 75atm, $H_2/CO=0.45$ and GHSV=3265 L(STP)/kg/hr on 0.4% CsOOCH promoted Cu/ZnO catalyst.

must be less than or equal to one, whereas the experimentally observed ratio is greater than one.

To correct the differences in predicted and observed selectivities described above, various modifications to the Vedage et al. proposal are required. The modifications are based on observations and experimental data reported in detail elsewhere (*1*) and briefly described below:

1) Methyl formate formation occurs via methanol carbonylation, which is at equilibrium for the conditions of the present investigation (*1*), and the parameter α_o is determined from the equilibrium constant. The methyl ester formation rates are written in terms of the parameter α_o' to improve the ester prediction at higher temperatures.

2) Two ß-addition rate constants are defined; one for the C_2 intermediate (β_1) and the other for higher carbon number intermediates (β_1') to correctly predict a 1-propanol/ethanol ratio greater than one.

3) Two and three carbon ß-addition is assumed to occur (β_2 and β_3), and this is consistent with experiments that show that ethanol and 1-propanol undergo coupling reactions, particularly at the lower temperatures, upon addition of these alcohols to the feed gas (*1*).

4) Insertion at a branched intermediate is assumed to be negligible and is ignored, consistent with an experiment which demonstrated that upon addition of 2-methyl-1-propanol to the feed gas, the yield of the anticipated insertion product, 3-methyl-1-

butanol, did not increase (*1*).

The proposed 5-parameter reaction network was presented in our previous quarterly technical progress report (4) and is illustrated in Figure 7. The distribution equations may be derived from the growth scheme as described previously (4) and applied to the measured product yield data by integrating the fixed-bed, plug-flow reactor equations. The model parameters were estimated by non-linear regression analysis, and the resulting predictions of oxygenate yields are compared to the measured values in Figures 8 and 9. The agreement between the measured and predicted values for ethanol, the C_5^+ alcohols, and the esters is significantly improved as compared with Figures 5 and 6.

The 5-parameter model is successful in describing the distribution of oxygenated products over a wide range of operating conditions. Estimates of the parameter values in the temperature range of 270°C to 310°C over the 0.4% CsOOCH promoted Cu/ZnO catalyst are given in Figure 10. From these data it is clear that, particularly at the higher temperature, ß-addition is significantly faster than insertion. The attainable higher alcohol selectivity is therefore limited by the slower insertion step, which is the first carbon-carbon bond forming reaction (to form ethanol) of the kinetic network. From the Arrhenius plots in Figure 10, the apparent activation energies for insertion and ß-addition ($ß_1$ at the C_2 species and $ß_1'$ at the higher alcohols) were estimated to be 33, 25, and 38 kcal/mol, respectively.

The 5-parameter model developed in the present investigation

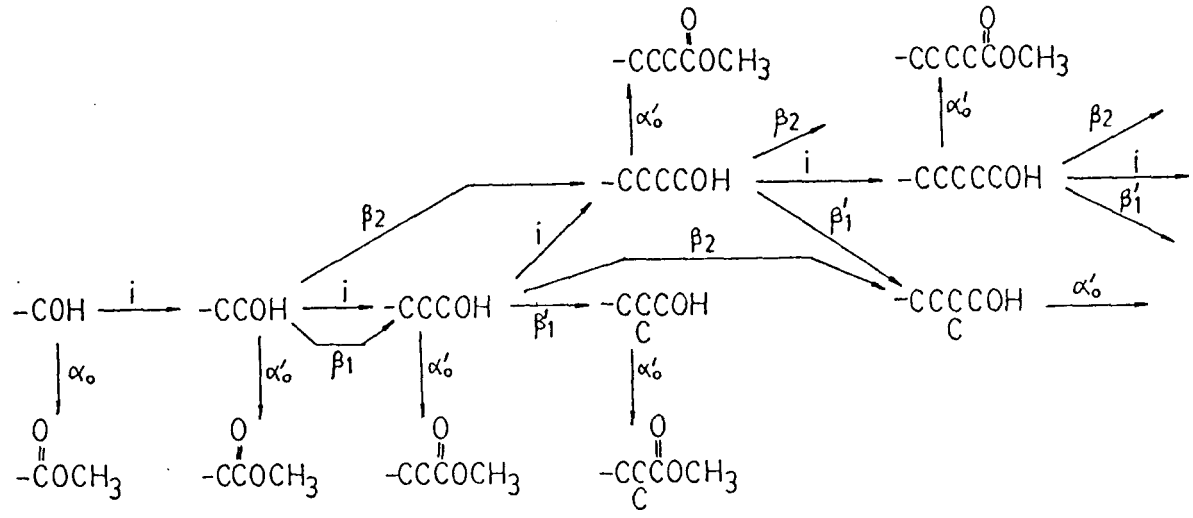


Figure 7: The 5-parameter reaction network for the synthesis of alcohols and methyl esters over alkali-promoted Cu/ZnO catalysts.

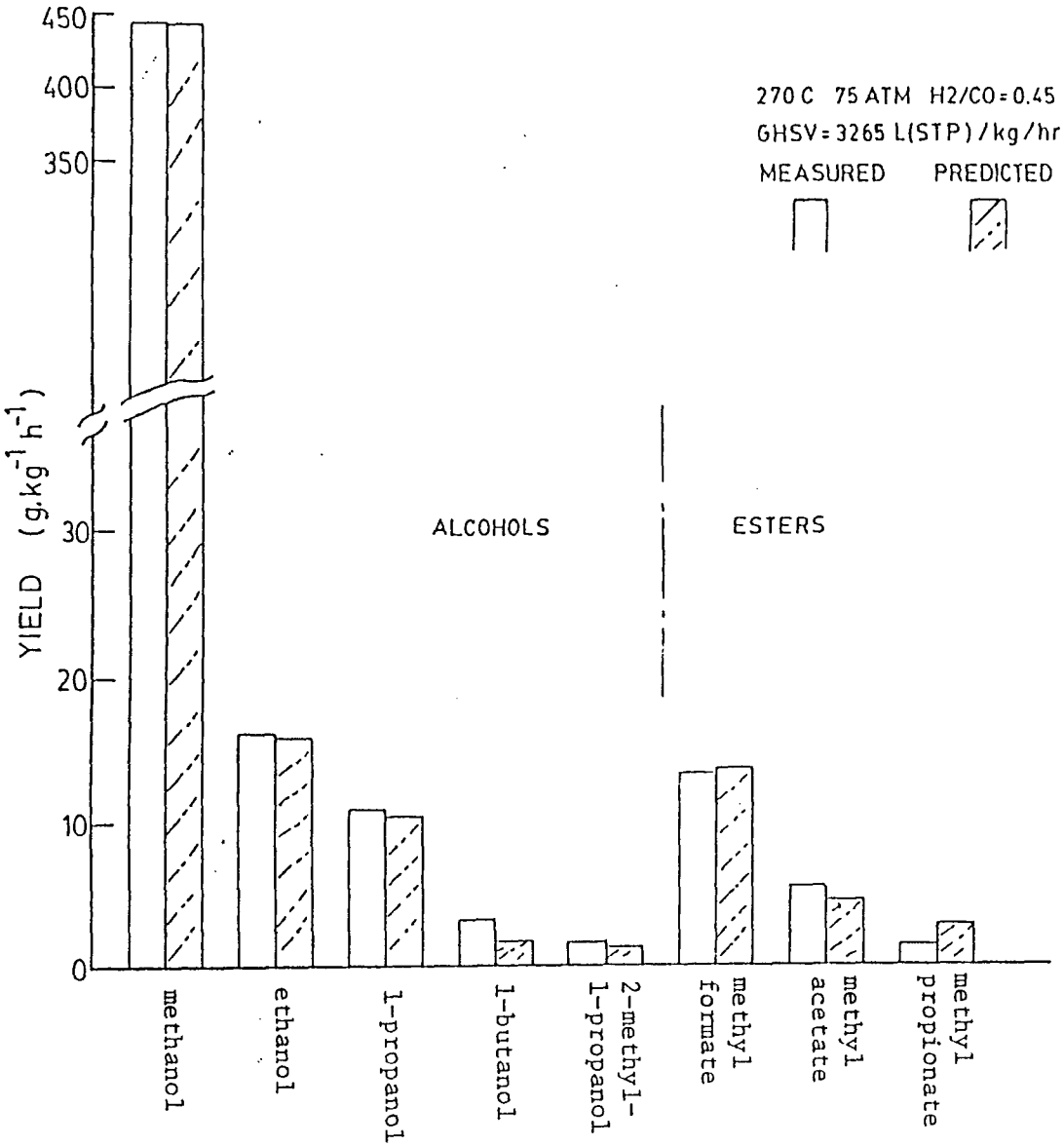


Figure 8 : Five parameter model applied to product yield data on 0.4% CsOOCH promoted Cu/ZnO catalyst at 270°C, 75 atm, $H_2/CO=0.45$, and GHSV=3265 l(STP)/kg/hr.

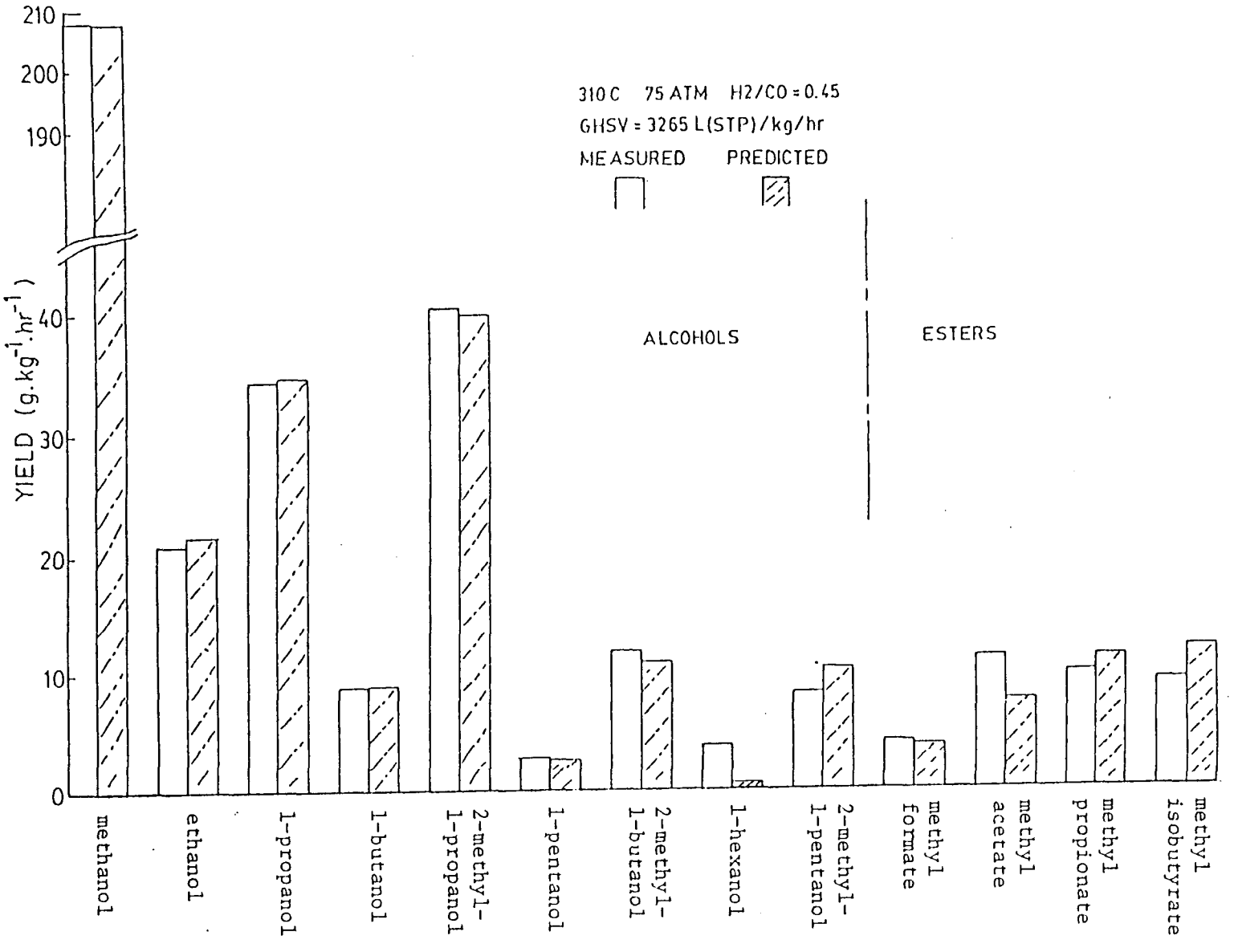


Figure 9: Five parameter model applied to product yield data on 0.4% CsOOCH promoted Cu/ZnO catalyst at 310°C, 75 atm, $H_2/CO=0.45$ and GHSV=3265 l(STP)/kg/hr.

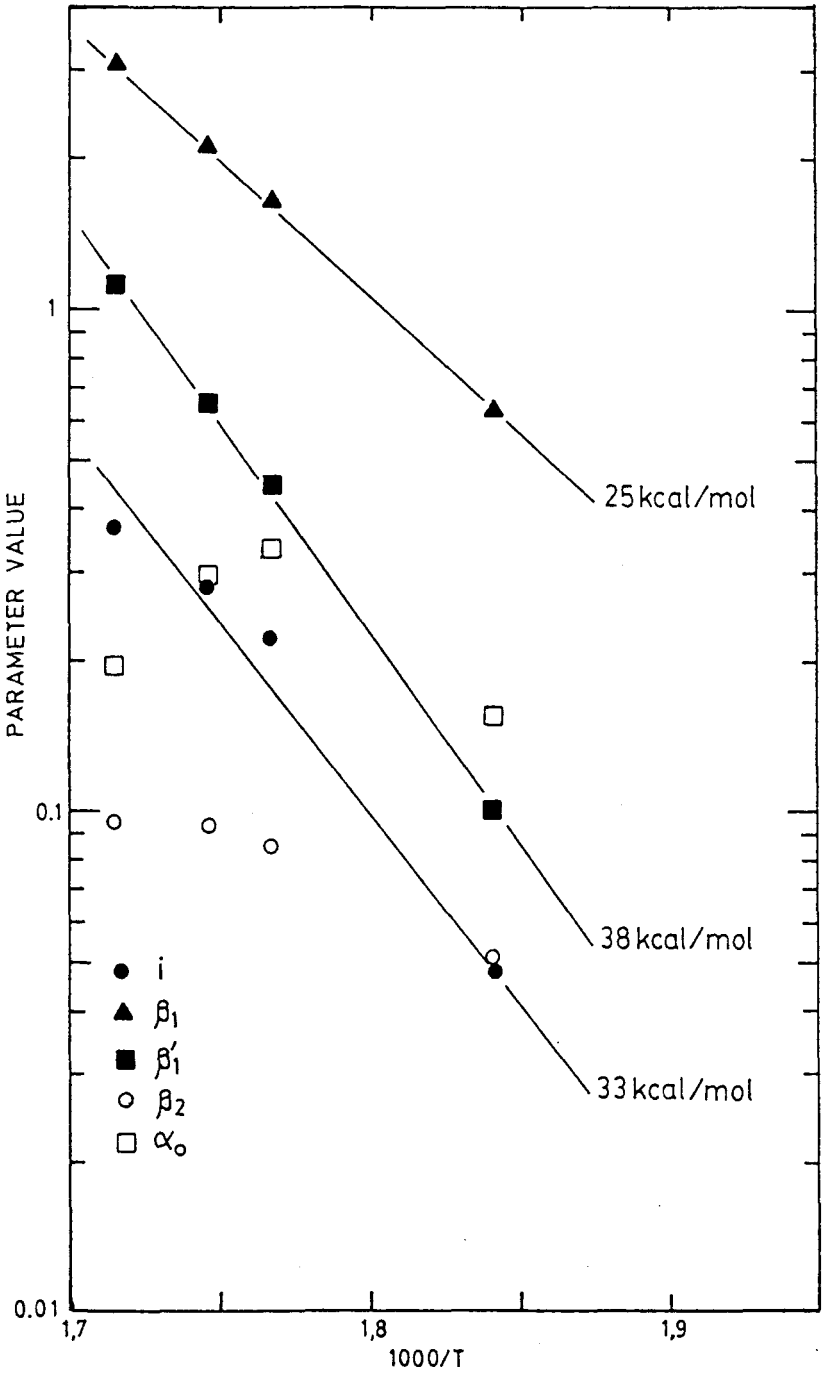


Figure 10: Arrhenius plots for parameters of the 5-parameter model for oxygenate synthesis on 0.4% CsOOCH promoted Cu/ZnO catalyst.

also successfully describes the effect of the gas hourly space velocity on the alcohol product distribution. Figure 11 compares the measured and predicted yields of the C_1-C_4 alcohols for a range of contact times (defined as the inverse of GHSV in seconds, where GHSV is in L(STP)/kg catalyst/hr). In this particular case, the model parameter values were estimated from an independent set of yield data measured at one particular contact time. Numerical solution of the integral, fixed-bed, plug flow reactor equations gives the predicted yields as a function of contact time. The measured values are in reasonable agreement with the model predictions, as shown in Figure 11. It is noted that in this case the difference between the measured and predicted values reflect not only the limitations of the model, but it also includes the overall measurement error.

The major objective in developing the kinetic model is to use it for prediction of operating conditions required to achieve desired methanol/2-methyl-1-propanol yields. Figure 12 gives an example of the predicted operating conditions required to achieve a methanol/(C_2-C_6) alcohol weight ratio of 70/30, the desired ratio for alcohol blending with gasoline. In this example, the H_2/CO feed ratio was restricted to 0.7 to reflect the typical synthesis gas composition from coal gasifiers, while the total reactant pressure was chosen as 90 atm to achieve a maximum higher alcohol yield. Figure 12 shows that the product yield will increase as the space velocity increases and as the reaction temperature decreases. To maintain the desired selectivity,

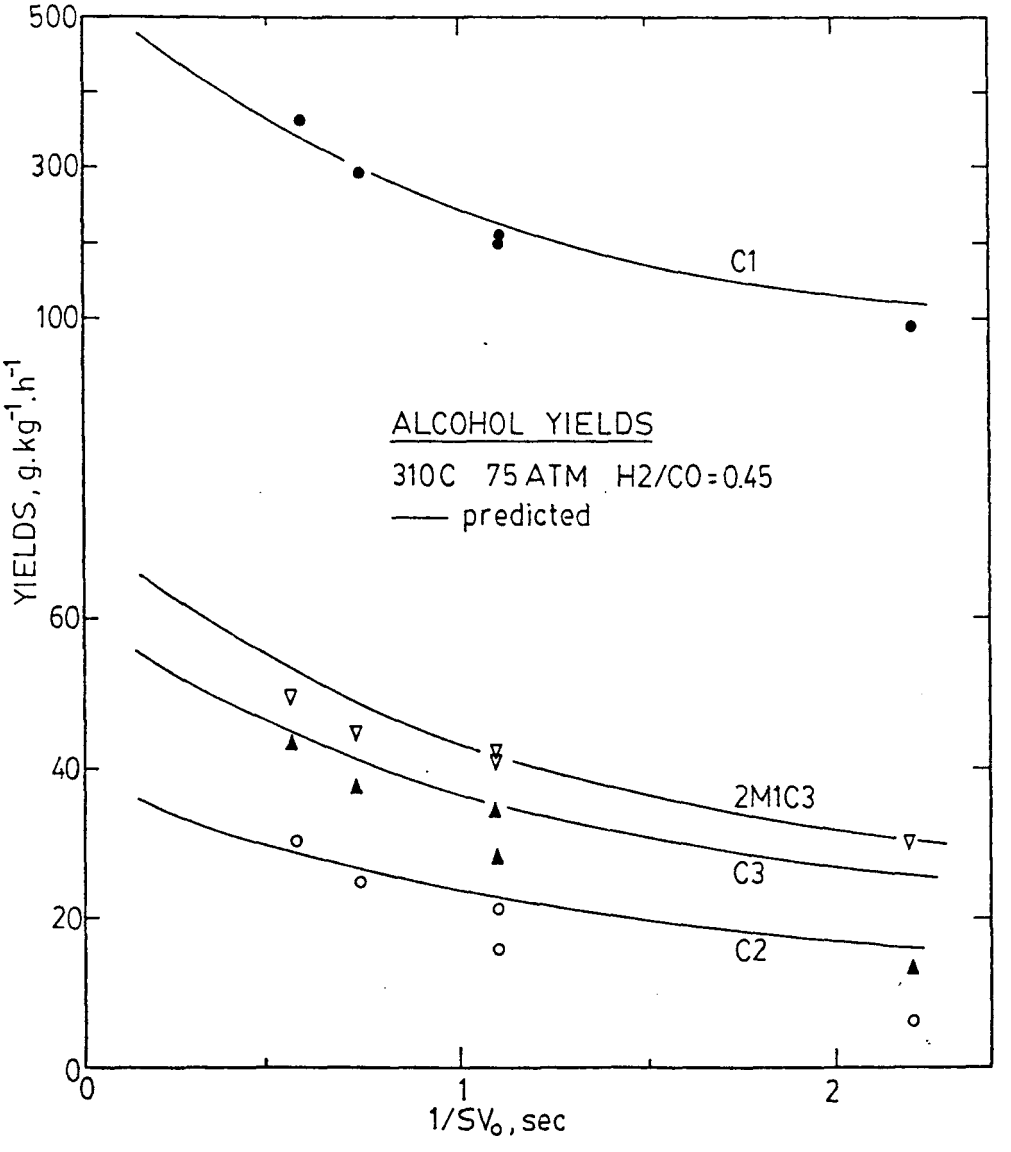


Figure 11: Predicted (full lines) and measured (●, methanol; o, ethanol; ▲, propanol; ▽, 2-methyl-1-propanol) alcohol yields as a function of contact time (defined as the inverse of the GHSV).

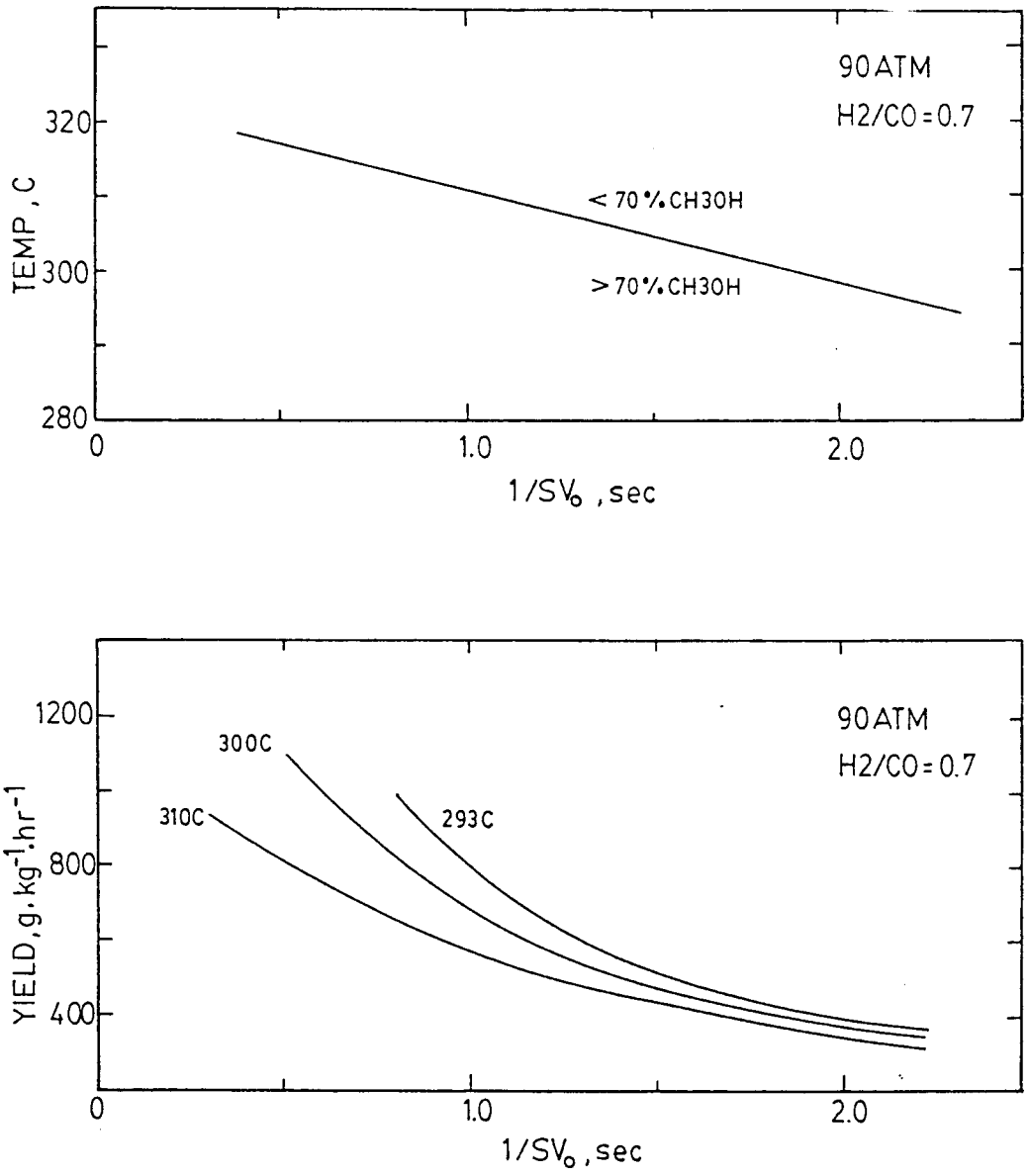


Figure 12: Model predictions of total C_1-C_6 oxygenate yields (bottom) and operating conditions required to obtain 70/30 mass ratio of $C_1/(C_2-C_6)$ alcohols (top) at 90atm and $H_2/CO=0.7$ on 0.4% CsOOCH promoted Cu/ZnO catalyst.

however, the temperature must be increased as the space velocity increases.

B) ^{13}C-Labelling studies of the alcohol synthesis

The reaction paths of the 5-parameter model developed above are based on observations regarding the oxygenate product distribution and the changes in product yields upon addition of alcohols to the feed gas. The results presented above show that the proposed reaction paths lead to successful predictions of the product distributions over a wide range of operating conditions. Further evidence for the reaction paths of the oxygenate synthesis has been obtained from experiments in which ^{13}C labelled alcohols have been added to the feed gas. The distribution of the ^{13}C in the product alcohols and esters indicate the reaction pathways for the incorporation of the added alcohols into the products formed over the 0.4 mol% Cs/Cu/ZnO catalyst. The concentration of the ^{13}C in the components of the product mixture were determined by NMR spectroscopy.

Figure 13 compares the ^{13}C-NMR spectra of the liquid product obtained upon addition of CH_3OH (natural abundance of ^{13}C) and $^{13}CH_3OH$ (enriched to 24% ^{13}C) to the synthesis gas for the conditions indicated. The data of Figure 13 show that upon addition of the labelled methanol, significant enrichment occurs for both carbons of ethanol, whereas only the methyl carbon of methyl formate is enriched. The data suggest that an active C_1-intermediate is formed from methanol that undergoes two reactions to form ethanol

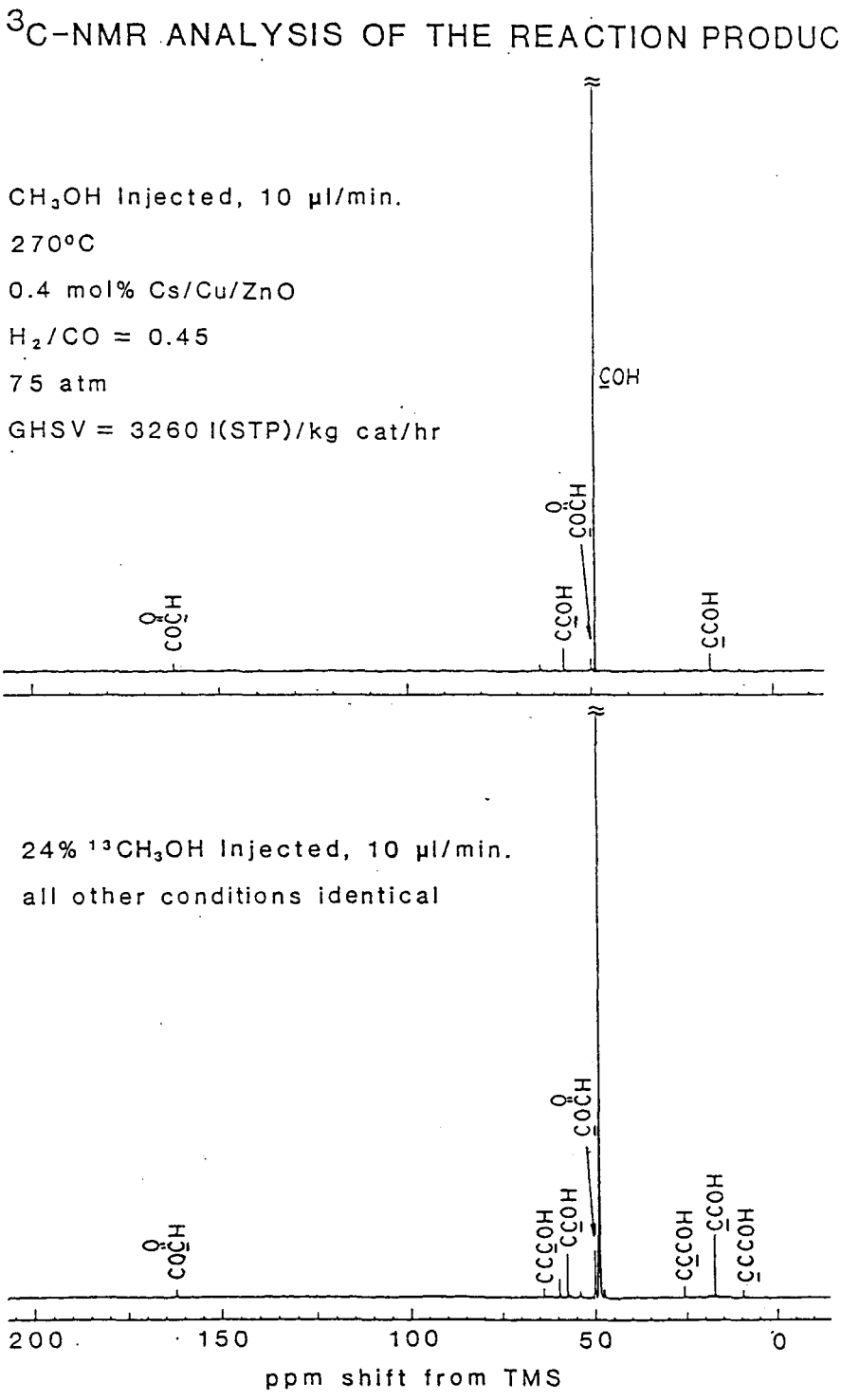


Figure 13: ^{13}C-NMR analysis of reaction product upon addition of CH_3OH (top) and $^{13}CH_3OH$ (bottom) at 270 C, 75atm, H2/CO = 0.45 and GHSV=3265 L(STP)/kg/hr and 0.4% CsOOCH promoted Cu/ZnO catalyst.

or methyl formate. Ethanol is formed by reaction of two oxygen-containing C_1-intermediates, whereas methyl formate is produced by carbonylation of the intermediate. These results are consistent with the reaction paths of the kinetic model described as insertion and α_o'.

A similar set of results are shown in Figure 14 for the case of CH_3CH_2OH and $CH_3{}^{13}CH_2OH$ addition to the $H_2/CO = 0.45$ feed gas. Upon the addition of labelled ethanol, significant enrichment of the carbons of 1-propanol, 2-methyl-1-propanol, and 1-butanol is observed. For 1-propanol, the greatest enrichment occurred at the 3-position carbon atom, whereas the 1-position carbon atom was not significantly enriched. According to the kinetic model developed above, the 1-propanol can be produced from ethanol by two reaction paths, insertion and ß-addition. The labelled ethanol addition experiment supports the proposed reaction path, provided that for ß-addition, the adding C_1-intermediate retains its oxygen in the final alcohol product. Thus, the 2- and 3-position enrichment of 1-propanol is a result of insertion and ß-addition, respectively. The kinetic model has shown that ß-addition is faster than the insertion step, which is in agreement with the observed greater enrichment of the 3-position carbon atom compared to the carbon located at the 2-position of 1-propanol.

The enrichment pattern of the carbons of the C_4 alcohols also supports the reaction paths of the kinetic model. According to the model, the major product of 1-carbon addition to 1-propanol would be 2-methyl-1-propanol via ß-addition, while the insertion

^{13}C-NMR ANALYSIS OF THE REACTION PRODUCT

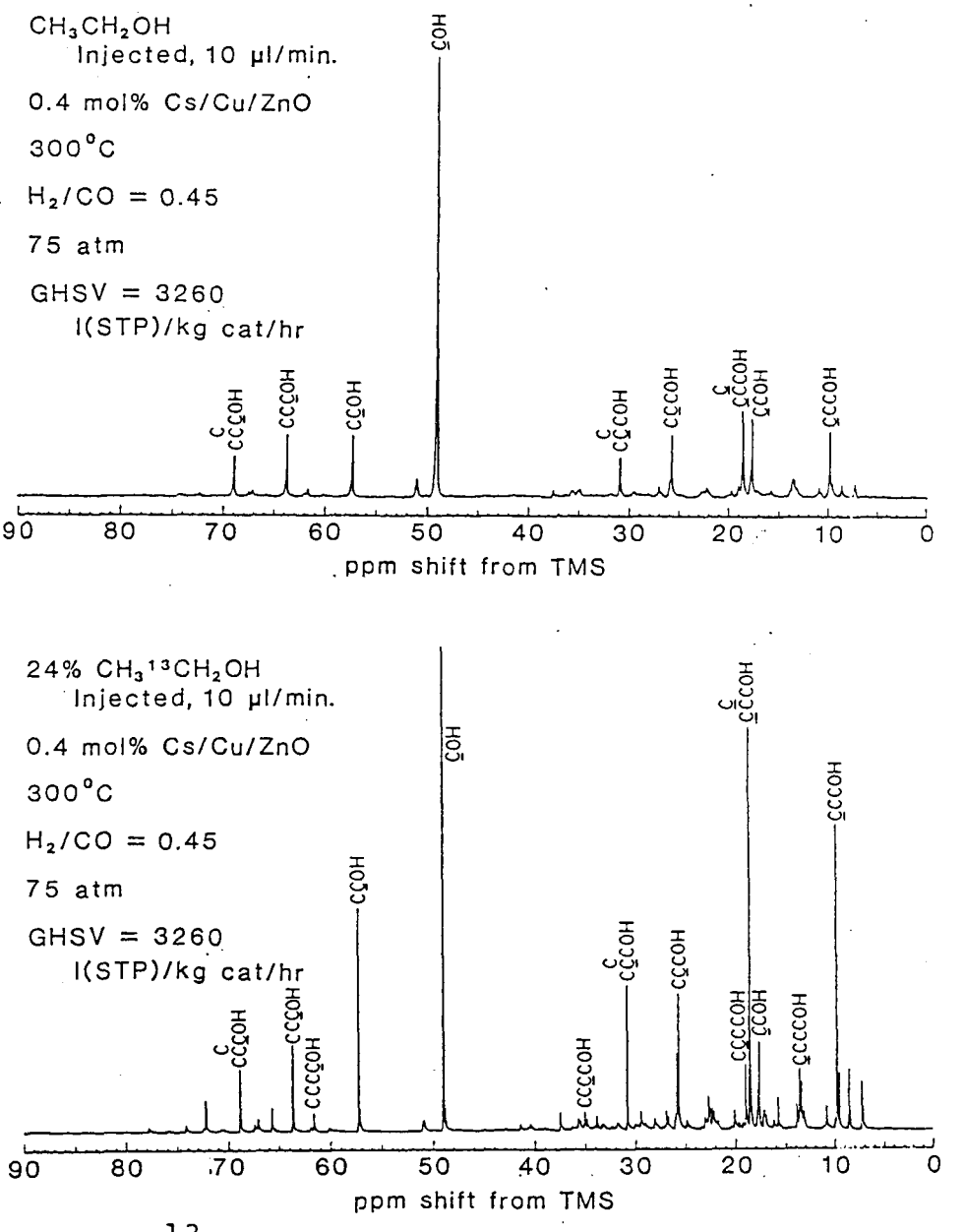


Figure 14: ^{13}C-NMR analysis of reaction product upon addition of CH_3CH_2OH (top) and $CH_3{}^{13}CH_2OH$ (bottom) at 300 C, 75atm, H_2/CO=0.45, GHSV=3265 L(STP)/kg/hr and 0.4% CsOOCH promoted Cu/ZnO catalyst.

product, 1-butanol, would be of less significance. For the C_4 alcohols, the greatest enrichment did experimentally occur at the carbons of the two methyl groups of 2-methyl-1-propanol, while a lesser degree of enrichment occurred at the 2-position carbon atom of 2-methyl-1-propanol. These enrichments are consistent with ß-addition to $^{13}CH_3CH_2CH_2OH$ and $CH_3{}^{13}CH_2CH_2OH$, the major components of 1-propanol that was formed by the injection of ethanol. Similarly, the enrichment observed for 1-butanol is consistent with the predicted products of C_1 insertion to the same labelled propanols.

C) Long-term activity test of the Cs/Cu/ZnO catalyst

A medium term activity test of the 0.4% CsOOCH promoted Cu/ZnO catalyst has also been completed. The conditions chosen for the test were estimated from the kinetic model, described in the previous section of this report, to maximise the alcohol yield and maintain a methanol/(C_2-C_6) alcohol weight ratio of 70/30. The results of the test are given in Figure 15.

The data show the catalyst to be stable up to about 250 hr, beyond which the activity began to decline. Analysis of the spent catalyst by chemical methods and by FTIR, photoacoustic, Auger, and X-ray photoelectron spectroscopies after 500 hr on stream showed the presence of iron, as well as a carbonaceous residue, on the catalyst. The unused catalyst was demonstrated to be free of iron. Analysis of the benzene-extractable carbonaceous residue showed it to be aliphatic linear long chain hydrocarbon. It is

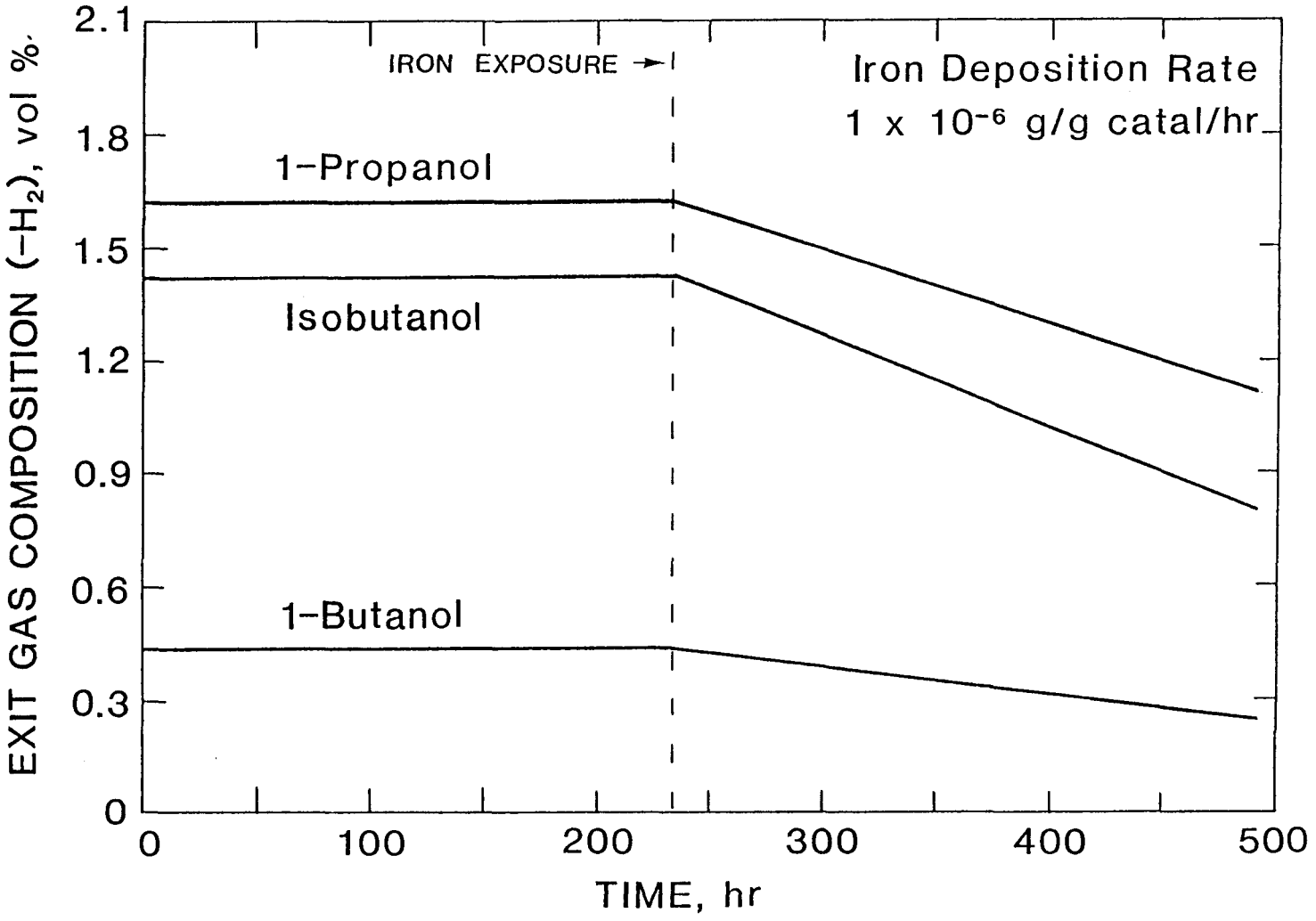


Figure 15: Deactivation profiles for propanol and butanols over 0.4% CsOOCH promoted Cu/ZnO catalyst at 295 C, 90atm, H_2/CO = 0.7 and GHSV = 3265 L(STP)/kg/hr.

concluded that the deactivation was induced by iron functioning as a surface site for polymeric chain growth, yielding a saturated hydrocarbon polymer that blocked the active synthesis portion of the catalyst. The iron was present in trace amounts in the synthesis gas as iron carbonyls.

To further demonstrate the poisoning effect of iron carbonyl on alcohol synthesis over these catalysts, a 0.4 mol% Cs/Cu/ZnO catalyst was tested under the same conditions as given in Figure 15, but where the iron carbonyl contamination was present at five times the concentration as before and was present from the beginning of the testing. The results of this test are shown in Figure 16 for the yields of 1-propanol, 1-butanol, and isobutanol. Analysis of both of these catalysts by X-ray powder diffraction showed that thermal sintering did not contribute to the observed deactivation. Additional precautions are being taken to ensure the complete removal of trace amounts of the iron carbonyl before carrying out the planned long-term activity tests of Cs/Cu/ZnO and Cs/Cu/Cr/ZnO catalysts.

CONCLUSIONS

A kinetic model for alcohol synthesis over a 0.4% CsOOCH promoted Cu/ZnO catalyst has been developed. There are two important kinetic steps incorporated in the model; a slow insertion step leading to linear alcohols and a faster ß-addition step that

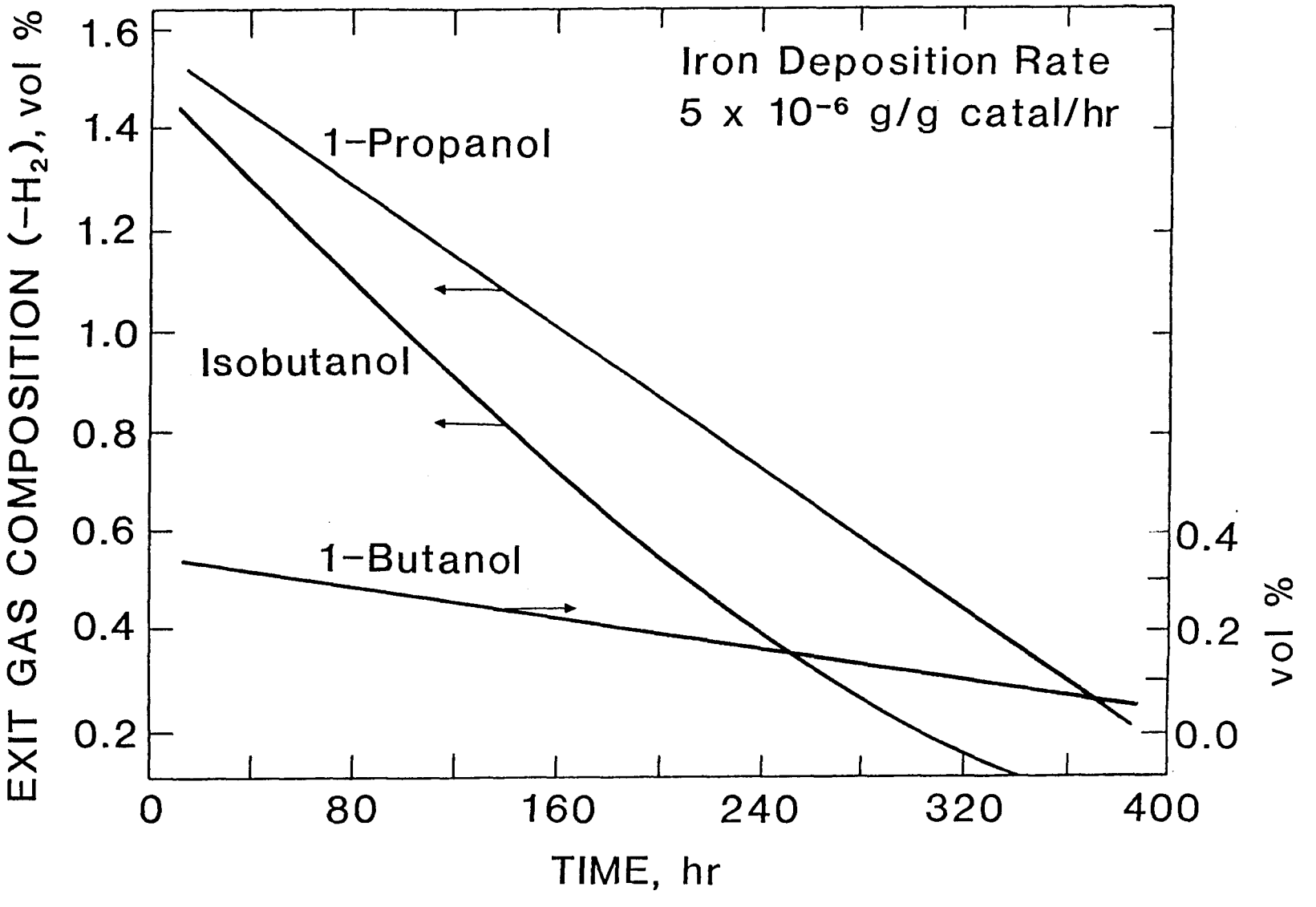


Figure 16: Deactivation profiles for propanol and butanols over 0.4 mol% Cs/Cu/ZnO catalyst as a function of iron deposition on the catalyst at 295°C and 90 atm with $H_2/CO = 0.7$ synthesis gas at GHSV = 3265 L(STP)/kg/hr.

yields branched alcohols. The first carbon-carbon bond forming step occurs via insertion to form ethanol, and this slow step limits the attainable higher alcohol yield. Branched 2-methyl higher alcohols are selectively produced because of the faster ß-addition step. Of less importance are 2- and 3-carbon ß-addition processes and the reaction pathway that produces methyl esters.

The model is applicable over a wide range of temperatures and space velocities and has been used to successfully predict operating conditions required to attain desired 2-methyl-1-propanol/methanol yields. Isotope labelling studies in which ^{13}C-labelled methanol and ethanol were added to the synthesis gas feed stream showed that the distribution of the ^{13}C in the product was consistent with the proposed sequence of steps in the kinetic scheme.

The medium term activity test for the 0.4% CsOOCH promoted Cu/ZnO catalyst showed that the catalyst was stable for up to 250 hr at 295^{o}C and 90 atm with a $H_2/CO = 0.70$ synthesis gas. Under these conditions, the total alcohol yield was 490 $g.kg^{-1}.h^{-1}$, while the methanol/(C_2-C_6) alcohol weight ratio was 70/30. Initial indications are that the catalyst deactivates because of trace amounts of Fe being deposited on the catalyst, and this results in build-up of a polymeric carbonaceous material that blocks the active part of the catalyst.

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