DEVELOPMENT OF ALTERNATIVE FUELS FROM COAL-DERIVED SYNGAS

R. P. Underwood, F. J. Waller and E. L. Weist

Air Products and Chemicals, Inc.
7201 Hamilton Blvd.
Allentown, PA 18195-1501

ABSTRACT

This paper reports on the status of (1) laboratory work in progress on the synthesis of mixed alcohols from syngas, (2) strategy for novel chemical methodologies to oxygenates from dimethyl ether and (3) initial understanding between octane numbers and compound structure.

Currently proposed processes for producing mixed alcohols from synthesis gas are based on conversion in packed bed reactors. However, a disadvantage of these packed bed reactor schemes is the difficulty in controlling the temperature rise produced by this highly exothermic conversion. Slurry reactors afford much better heat management capabilities, thus allowing for potentially better catalyst stability, a higher conversion per reactor pass, and the ability to process high CO/H_2 ratio syngases derived from coal. In the present work, slurry-phase synthesis of mixed alcohols had been investigated using a continuous, micro-autoclave reactor system.

An alternative route to mixed ethers uses dimethyl ether, which is being actively considered as a building block for transportation fuel additives. Reaction methodologies based on oxidative coupling, vinylation and/or carbonylation are being evaluated in the laboratory.

It is possible that economic-alternative compounds could surface in the future. In order to facilitate the screening of oxygenate candidates for U. S. gasoline, better predictive modelling tools are necessary to establish structure vs. octane number correlations. Initial results in this area point to the need for future computational chemistry modelling.

OBJECTIVE

To test existing technologies or develop new methodologies for the conversion of synthesis gas or dimethyl ether into oxygenates, in particular, ethers for transportation fuels. To demonstrate at least one of these processes at a semi-works scale in DOE's LaPorte Alternative Fuels Development Unit (AFDU).

INTRODUCTION

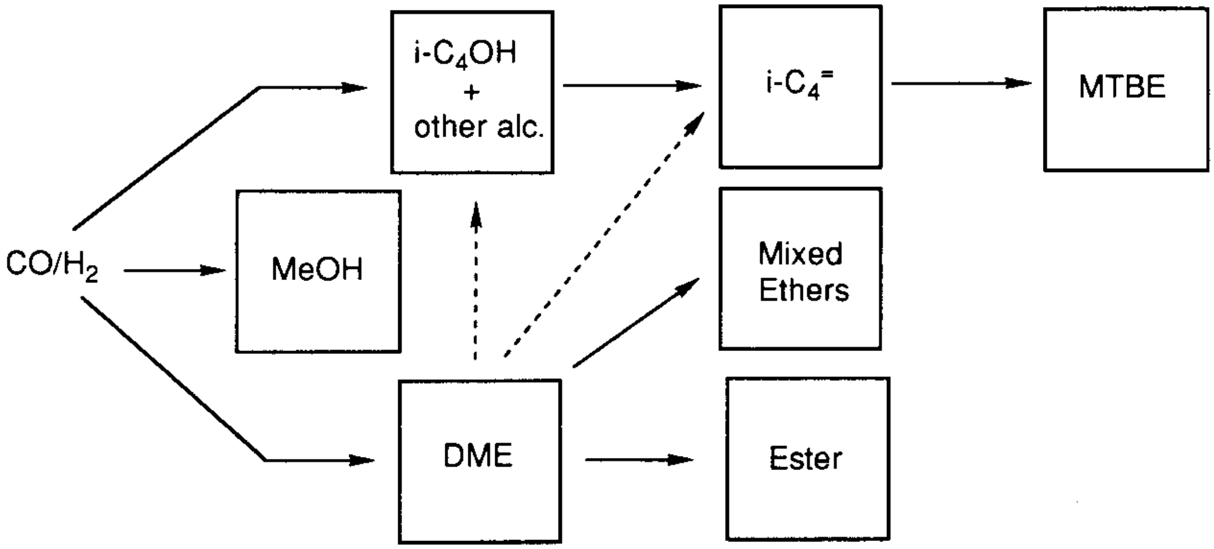
Prior to 1980, the oil industry had little interest in oxygenated fuels as a component of gasoline. Removing lead from gasoline and searching for suitable replacement octane enhancers made U. S. refiners move decisively in the direction of MTBE as the preferred oxygenate for gasoline blending. Presently, the petrochemical industry is rapidly expanding MTBE capacity to meet projected market demand following Clean Air Act regulations. The Clean Air Act now requires that nearly 25% of the U. S. gasoline contains oxygenates by 1995.

Currently, the MTBE capacity is 5.6 million metric tons with capacity to double to over 14 million metric tons by 1995 (1). All MTBE is manufactured from isobutylene and methanol. The isobutylene either from fluid catalytic cracking facilities or dehydrogenation routes from butanes has its origin from foreign energy sources.

ALTERNATIVE FUELS I

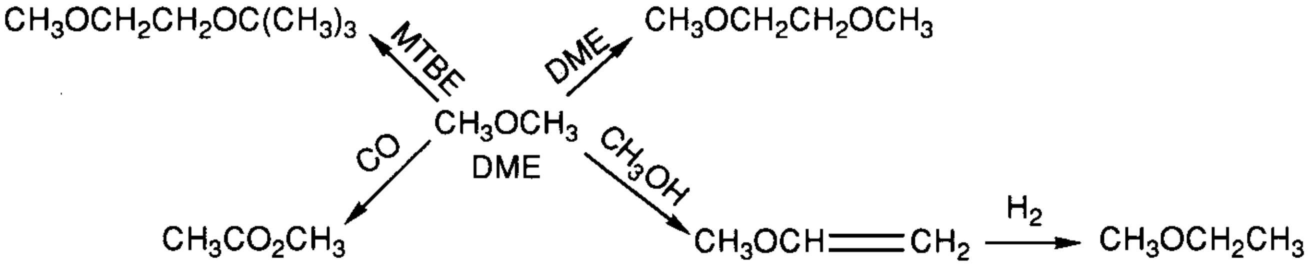
As the market for fuel oxygenates continues to grow, there will be increased opportunities for other oxygenates. Of particular interest is the production of oxygenated fuels from non-petroleum sources, such as coal-derived synthesis gas. Possible oxygenates from synthesis gas are MTBE, mixed alcohols, mixed ethers derived from mixed alcohols or oxygenates from the building block dimethyl ether (DME). These alternatives could serve not only as a blending component for gasoline but also as a cosolvent for methanol. Examples of classes of alternative candidates from DME are diethers, acetates and alcohols.

The overall approach to MTBE and other oxygenated fuels under Alternative Fuels I is outlined in Scheme 1. Slurry-phase synthesis of mixed alcohols from coal-derived synthesis is planned for the February 1992 campaign at LaPorte. In addition, dimethyl ether is being considered as a



Scheme 1. Coal-Derived Oxygenated Transportation Fuels

building block for transportation fuel additives such as mixed ethers or esters. In fact, DME has potential for many reaction pathways. Several of these pathways are represented in more detail in Scheme 2 (2). Reaction methodologies based on oxidative coupling, vinylation and carbonylation are being evaluated in the laboratory. These methodologies allow connecting pathways to alcohols, mixed ethers and alkyl esters.



Scheme 2. Potential DME Reaction Chemistry

SYNTHESIS OF MIXED ALCOHOLS

Background

Alcohols are known to be effective oxygenated gasoline components. Table 1, which shows the average of the research and motor octanes for some alcohols (3), indicates that C_1-C_4 alcohols are good octane improvers.

Table 1

Average Blending Octane Numbers for Selected Alcohols

Alcohol	Blending Octane (R + M)/2
methanol	115
ethanol	113
1-propanol	105
isobutanol	101

Studies have also shown that the use of mixed alcohols in gasoline results in lower hydrocarbon and CO emissions at the tailpipe (4). However, a potential drawback is that alcohols in gasoline are sensitive to phase separation in the presence of water, which is ubiquitous in the gasoline distribution system. Alcohol blends with a high methanol content are particularly sensitive to this phase instability. For the effective use of alcohols as a gasoline additive, a considerable fraction of C_{2+} cosolvent alcohols is necessary for phase stability in the presence of H_2O. Thus, a commercially viable process for the production of mixed alcohols from syngas must have a relatively high selectivity to C_{2+} cosolvent alcohols.

Existing proposed processes for the production of mixed alcohols from syngas are based on conversion in packed bed reactors (5-6). However, the conversion of syngas to alcohols is highly exothermic. Table 2 shows the heats of reaction for the synthesis of selected alcohols from CO and H_2.

Table 2

Heats of Reaction for Synthesis of Selected Alcohols from CO and H_2

$$xCO + 2xH_2 \longrightarrow C_xH_{(2x+1)}OH + (x-1)H_2O$$

$C_xH_{2x+1}OH$	ΔH_{rxn} (@298°K), kcal/mole
methanol	-17
ethanol	-53
1-propanol	-85
isobutanol	-131

The heat of reaction per mole of product alcohol increases substantially with molecular weight. Removal of this high reaction heat is difficult in packed bed reactors. Slurry reactors offer much better heat management capabilities enabling a higher per-pass conversion, potentially better catalyst stability through the elimination of "hot spots", and the ability to process unshifted synthesis gas. Another potential advantage in the use of a slurry reactor is an enhancement in the selectivity to higher alcohols induced by secondary conversion, eqn. 1,

$$\text{lower alcohols} \xrightarrow{CO/H_2} \text{higher alcohols} \qquad (1)$$

as a result of reactor backmixing.

The purpose of the present study was to investigate slurry-phase mixed alcohols synthesis on a lab scale. A modified $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst was used in a stirred autoclave reactor with mineral oil as the liquid medium. Syngas ($CO/CO_2/H_2$) was converted in a "once-through" mode. The effects of temperature, gas-hourly space velocity, and feed composition were investigated.

Experimental

The feed gases were obtained from premixed cylinders. The syngas compositions, which are shown in Table 3, simulate the typical product from Texaco or Shell coal gasifiers.

Table 3

Composition of Syngases

Gasifier	CO	H_2	CO_2	N_2
Shell	66	30	3	1
Texaco	51	35	13	1

The feed gas flow rate to the reactor was controlled by electronic mass flow controllers, while exit flow rate was measured by a wet test meter. Reactor pressure was controlled by a back pressure regulator. All lines downstream of the reactor were heat-traced to prevent the condensation of reaction product vapors. A gas-liquid separator was used to return vaporized mineral oil to the reactor. In some experiments, methanol and ethanol were added to the syngas feed by means of a high-pressure syringe pump, which injected the liquid alcohol to a heated feed vaporizer located immediately upstream of the reactor. The reactor used was stirred micro-autoclave manufactured by Autoclave Engineers. The internal volume of the reactor is 50 cm^3 and is constructed of Hastelloy C-276.

The catalyst used was a $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst, in powder form, which has been modified using a proprietary procedure. A typical reactor charge was 4.25 g of catalyst and 17.0 g of Pennreco Drakeol 10, a white mineral oil consisting of paraffinic and naphthalenic hydrocarbons. The oil has been shown to be stable in the presence of the catalyst at the high temperatures used for mixed alcohols synthesis. Catalyst activation was carried out in the reactor using an activation gas of 2% H_2/98% N_2.

Product analysis was done on-line by two gas chromatographs. Bulk gas analysis was done by one GC equipped with dual TCDs, while the organic products were quantified by a second GC outfitted with an FID and a capillary column.

Results and Discussion

Effect of Gas-Hourly Space Velocity:

Figure 1 shows the effect of gas-hourly space velocity (GHSV) on the synthesis rates of methanol and C_2-C_6 alcohols for the modified $Cu/ZnO/Al_2O_3$ catalyst. In this paper, GHSV is defined as the ratio of volumetric flow rate of feed gas standard conditions (0°C and 1 atm) to the mass of catalyst and has units of std. lit./kg-hr. For Shell gas at 300°C and 7.0 MPa, the methanol rate increases linearly with GHSV. In fact, the reactor exit methanol concentration is approximately invariant with GHSV, indicating that the methanol synthesis reaction is at equilibrium across this range of GHSV. Thermodynamic equilibrium calculations incorporating the reactor exit gas concentrations support this contention. The C_2-C_6 alcohols rate increases monotonically with GHSV, but unlike the result for methanol, the rate is non-linear. The measured rate for C_2-C_6 alcohols is not constrained by thermodynamic limitations at these reaction conditions. Instead, the formation rate is governed by the intrinsic reaction kinetics. At 10,000 GHSV, the rate of formation of C_2-C_6 alcohols is 129 g/kg-hr, the highest rate observed at 300°C and 7.0 MPa.

Selectivities calculated from the results of the experiments used for Figure 1 are shown in Figure 2. The selectivity is based on the total organic product and does not include the CO_2 produced from CO via the water-gas shift reaction. The selectivity to C_2-C_6 alcohols decreases, while the selectivity to methanol increases, with increasing GHSV. The primary reason for this behavior is that the conversion to methanol is limited by thermodynamic equilibrium at all GHSV in the range investigated. Selectivity to total alcohols in these experiments is greater than 93%. The major non-alcohol organic products are methyl formate, methyl acetate, and methane.

Higher productivity and selectivity may be expected upon simultaneous optimization of the catalyst and the operating conditions.

Alcohol Product Distribution:

Figure 3 shows the distribution of alcohol products obtained using Shell gas at 300°C, 7.0 MPa, and 5,000 GHSV. The alcohol products are largely primary alcohols. Among the C_2-C_6 alcohols, isobutanol is produced in the highest selectivity, approximately 9 wt. %. In fact, for a given C_n alcohol, the selectivity to the "2-methyl" isomer is much greater than for the linear isomer. This has been observed for $Cu/ZnO/Al_2O_3$-based higher alcohols catalysts by other workers (7-8). To explain this type of product distribution, Klier et al have postulated a surface reaction mechanism which proceeds through a β-ketoalkoxide intermediate (8).

They have termed the mechanism "aldol coupling with oxygen retention reversal". The same type of mechanism is probably operative in the present system, though there is no direct evidence that this is the case.

Effect of Syngas Composition:

The effect of synthesis gas composition on the product alcohol rate is shown in Figure 4, which is a comparison of the results obtained for Texaco and Shell gas feed. The C_2-C_6 alcohols rate is much higher for Shell gas than Texaco gas. In addition, the relative difference is larger at the higher GHSV. At 10,000 GHSV, the C_2-C_6 alcohols rate for Shell gas is 80% higher than that for Texaco gas. The reason for the greater C_2-C_6 alcohols rate observed for Shell gas is not immediately clear. One possibility is the lower CO_2 content (3 mol % for Shell vs. 13% mol for Texaco).

Effect of Reaction Temperature:

Figure 5 shows the effect of reaction temperature on the product selectivity of the major products from Shell gas at 7.0 MPa and 5,000 GHSV. Between 280°C and 320°C, the methanol rate decreases monotonically with temperature, reflecting the constraint that thermodynamic equilibrium imposes on that synthesis reaction. By contrast, the C_2-C_6 alcohols rate is less influenced by temperature over the same temperature range. The highest C_2-C_6 alcohols rate was observed at 300°C, while the greatest selectivity to these products was observed at 320°C, the highest temperature used.

The influence of temperature on the rate of synthesis of the major C_{2+} alcohol products, ethanol, 1-propanol, and isobutanol, is rather interesting. The ethanol rate decreases with temperature across the range, while the isobutanol rate increases. The rate for 1-propanol is relatively invariant with temperature. Unlike the methanol synthesis reaction, syngas conversion to ethanol and 1-propanol at these reaction conditions is not constrained by thermodynamic equilibrium. Across this range of temperature, the rates for ethanol and 1-propanol are quite far from the equilibrium values. Thus, the decrease in rate with temperature, as observed for ethanol, must be attributed to some other phenomenon. The decrease in ethanol rate and simultaneous increase in isobutanol rate with increasing temperature suggests that secondary conversion of ethanol to isobutanol occurs at a faster rate than ethanol formation and this reaction becomes more significant at higher temperature. The possibility that ethanol undergoes secondary reaction to isobutanol is supported by the following results.

Formation of Higher Alcohols from Lower Alcohols:

Support for the concept of the involvement of lower alcohols in secondary reactions to produce higher alcohols is provided by the results in Table 4, which shows the effect of methanol and ethanol addition to the syngas feed. In these experiments, methanol and ethanol were added to the syngas feed as vapors, a situation which simulates recycle of methanol and ethanol product. Both alcohols were added to Shell gas feed, flowing at 5,000 GHSV, at a level 5 mol %. The corresponding rates of methanol and ethanol addition are 376 g/kg-hr and 540 g/kg-hr, respectively.

Table 4

Effect of Methanol and Ethanol Addition to Syngas Feed

	Rate (g/kg-hr)				
Feed	methanol	ethanol	1-propanol	isobutanol	ΣC_3-C_6 Alcohols
Shell	243	15	15	26	63
Shell + 5 mol % methanol	361	21	20	29	76
Shell + 5 mol % ethanol	241	116	64	55	162

As shown in Table 4, the addition of 5 mol % methanol to the syngas feed has a minor effect on the rates for higher alcohols, with only a modest increase in the rate for C_3-C_6 alcohols. A large fraction of the added methanol did not undergo conversion in the reactor, as revealed by the increase in methanol rate upon methanol addition. Also, a material balance indicates that a substantial portion of the added methanol decomposed to CO and H_2, presumably through the reverse of the methanol synthesis reaction. This is not surprising since the methanol synthesis reaction is at equilibrium.

In contrast to the results for methanol addition, the addition of 5 mol % ethanol to the feed dramatically increases the rate of synthesis of C_3-C_6 alcohols. Upon ethanol addition, the 1-propanol rate increases by a factor of 3, while the isobutanol rate increases by twofold. The rate to all C_3-C_6 alcohols increases by almost a factor of three with ethanol addition.

Conclusions

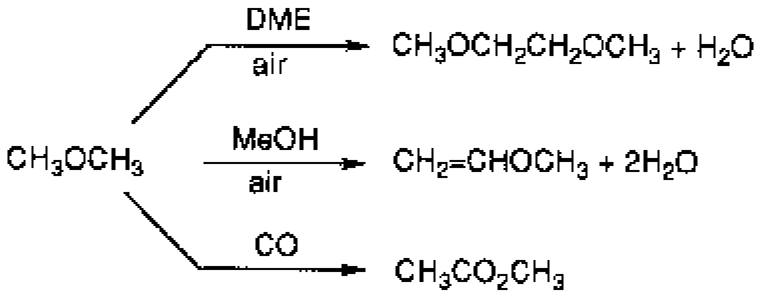
Slurry-phase mixed alcohols synthesis from syngas has been successfully demonstrated on a lab scale. The use of a modified $Cu/ZnO/Al_2O_3$ methanol catalyst has resulted in a reactor productivity as high as 600 g/kg-hr for mixed alcohols synthesis from simulated coal-derived syngas. The alcohol product obtained, even for once-through operation, contains a large fraction of C_{2+} alcohols and is potentially suitable for gasoline blending. In addition, reaction temperature has a large effect on the alcohol product slate; the selectivity shifts to isobutanol with increased temperature. The secondary reaction of methanol and ethanol to produce C_{3+} alcohols was observed by addition of these alcohols to the syngas feed.

DIMETHYL ETHER AS A BUILDING BLOCK

Background

With dimethyl ether (DME) as a starting point in any viable economic process, novel methodologies are required to selectively activate the methyl group of DME. Ethers, in general, are thought to be chemically inert except for cleavage by HI or the dehydration of DME to ethylene. Highly branched ethers with adjacent CH bonds to oxygen are susceptible to peroxide formation.

Specific enabling technologies require selective catalysts for oxidative coupling, vinylation and carbonylation. Examples of thermodynamically allowed transformations starting with dimethyl ether are summarized in Scheme 3. The 1,2-dimethoxyethane and/or methyl vinyl ether can in turn, act as building blocks to higher molecular weight ethers. Table 5 summarizes ΔG_{rxn} for each of the proposed methodologies in Scheme 3. In each example, the methyl group is activated by an adjacent methoxy group. The ease of CH_3 activation should be reflected by the strength of the CH bond. One such measure of the CH bond strength is the pK_a of the corresponding acid. Several model compounds are shown in Table 6. The relative



Scheme 3. DME Methodologies

Table 5

Gibbs Energy Change for Proposed Methodology

Methodology	ΔG_{rxn} (@ 473°K, kcal/mole)
Oxidative coupling	-45.6
Vinylation	-58.0
Carbonylation	-14.8

Table 6

Acidity Scale for Selected Compounds

Compound	Approximate pK_a (relative to water)	Reference
$H\text{-}CH_2CH_3$	42	9
$H\text{-}CH_3$	40	9
$H\text{-}CH_2C_6H_5$	35	9
$H\text{-}CH_2OCH_3$	?	----
$H\text{-}CH_2CN$	25	10
$H\text{-}CH_2CO_2R$	24	9
$H\text{-}CH_2CO_2H$	24	10
$H\text{-}CH_2COCH_3$	20	10

position for DME should not change if CH bond cleavage occurs either heterolytic or homolytic.

Several literature references illustrate the progress other researchers have made in this area. Dimethyl ether has been oxidatively coupled to 1,2-dimethoxyethane at 200°C and 16 atm over a catalyst consisting of 20% wt. loading of SnO_2 on MgO. With a DME/O_2 mol ratio of 5, the DME conversion is 1-10% with dimethoxyethane selectivity of 60%. Vinylation or cross-coupling reactions between methyl propionate and methanol, acetone and methanol, acetonitrile and methanol to yield methyl methacrylate, methyl vinyl ketone and acrylonitrile respectively have been reported. In each case, MgO was modified by transition metal cations, calcined and then tested at 350°C for catalytic activity. Table 7 summarizes results with methanol. When in the presence of gaseous oxygen, the methanol is oxidized to formaldehyde and finally reacts with the activated methyl group. However other reaction mechanisms may be operative but the overall net effect is the same.

Table 7

Vinylation of Selected Compounds with Activated Methyl Groups

Reaction	Catalyst	Conv.	Sel.	Reference
$CH_3CH_2CO_2CH_3$+ CH_3OH	Mn/MgO (16.7%)	10.2	60.8	11
CH_3COCH_3 + CH_3OH	Fe/MgO (3.1%)	12.1	54.5	12
CH_3CN + CH_3OH	Cr/MgO (3.1%)	9.6	94.2	13

Laboratory results

During the first year, the laboratory program has been focused on reactor procurement and installation, Process Hazards Reviews dealing with oxidative chemistry, catalysts preparation and initial screening experiments on oxidative coupling and vinylation.

Presently, two reactor systems have been installed for catalyst evaluations. The first system is a dual atmospheric gas-phase reactors with 0.5 inch diameter heated by a tube furnace inside a temperature controlled oven. Oxygen, nitrogen and dimethyl ether are metered by electronic mass flow controllers and methanol by syringe pump. A process flow diagram is shown in Figure 6. On-line GC consists of two injectors, A and B. On injector A, a 100 µl sample passes through a 6" column of Hayesep D to adsorb heavy organics before a 10 foot column of Carbosieve II separates the light gases. On returning to the load position, the organics are desorbed from the Hayesep D precolumn with a temperature ramp. On injector B, a 10 µl sample loop does direct injection to a 15 meter megabore column with 5 µm film of polydimethylsiloxane (AT-1). The column oven limit is set at 225°C - the maximum temperature for the Carbosieve column.

The second system is a Autoclave Engineers' Bench Top Reactor System (BTRS). One to thirty cm^3 of catalyst can be placed on a wire mesh supported inside either a 0.312" or 0.515" ID tubular reactor of stainless steel. Each 18" reactor is heated by a tube furnace with three 4" heated zones which is placed inside a temperature-controlled oven. Nitrogen and an oxygen/nitrogen mixture are metered by electronic mass flow controllers. HPLC pumps and/or high pressure syringe pumps deliver liquid reactants which are added to the heated nitrogen stream inside another temperature-controlled oven. The reactor effluent passes through a gas-liquid separator with manual drain. The pressure of the reactor is adjusted up to 1500 psig using an electronic back pressure regulator. Analysis of the gaseous reactor effluent is effected using on-line gas chromatography. The reactor and oven temperature, gas and liquid flow rates, and reactor pressure are controlled by an Autoclave Engineers Model 900 Process Controller. The Process Controller monitors for high temperature, high pressure, and high flow, and for failsafe shutdown of the unit. A combustible gases detector is connected to the controller for shutdown.

Catalyst Model

Heterogeneous catalysts screened are based on the working catalytic model requiring a redox metal ion on a basic support for activation of the CH bond of CH_3OCH_3. Literature references cited in this paper illustrate starting points for the preparation of such catalysts.

Conclusions

To date, reactor systems have been installed in the laboratory to safely evaluate catalysts under oxidative conditions. A working catalyst model has been proposed, and presently heterogeneous catalysts have been prepared and are actively being evaluated for reaction pathways summarized in Scheme 1.

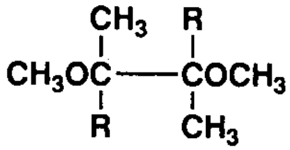
STRUCTURE VS. OCTANE NUMBER CORRELATIONS

There have been limited reports on extensive fuel property blending values of oxygenated additives for transportation fuels. With available literature values and our own evaluation of RON and MON properties of fuel mixtures, Table 8 can be constructed illustrating the importance of a stable fragment for the non-alcohol additives. It must be remembered that blending variations depend on hydrocarbon composition, octane level of the base gasoline as well as the concentration of the additive. Does this suggest that highly branched diether additives, such as the one shown below where R=H or CH_3,

Table 8

Blending Octane Numbers of Non-Alcohol Additives

Additive	Blending (R + M)/2 of Additive	Reference
MTBE	109	14
ETBE	110	14
methyl acetate	101	15
ethyl acetate	105	16
dimethyl carbonate	99	17
diethyl carbonate	108	18



$$CH_3O\underset{R}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{R}{C}}OCH_3$$

will have desirable blending properties in gasoline?

FUTURE PLANS

The next campaign at LaPorte will be the synthesis of mixed alcohols from syngas. Developmental work on the conversion of dimethyl ether to a transportation fuel additive has been initiated with an economic evaluation set for July '92. Computational chemistry software evaluation for modelling the correlation between octane numbers with structure is set for 1QFY92.

ACKNOWLEDGEMENTS

The research described here was supported in part under contract from the U. S. Department of Energy. The authors are grateful to D. M. Brown, T. H. Hsiung, J. F. Hugo, G. W. Long and D. J. Bieak for their contributions toward this work. Special thanks to N. R. Leiby for typing the manuscript.

REFERENCES

1. *Clean Air Drives the MTBE Race*, Chemical Week, pp. 22-23, July 31, 1991.

2. *Dimethyl Ether from Syngas in One Step*, C&EN, pp. 20-21, July 22, 1991.

3. F. W. Cox in *Proceedings of the Third International Symposium on Alcohol Fuels Technology*, II-22, pp. 1-14, U. S. Department of Energy, Asilomar, CA. 1979.

4. API Publication 4261, *Alcohols and Ethers - A Technical Assessment of Their Application as Fuels and Fuel Components*, 2nd Edition, July 1988.

5. Ph. Courty, P. Chaumette, C. Raimbault and Ph. Travers, *Production of Methanol-Higher Alcohol Mixtures from Natural Gas via Syngas Chemistry*, Revue de L'Institut Francais de Petrole **45**(4), July-August 1990.

6. S. Uchiyama and N. Kawate, *Production of Mixed Alcohols from Synthesis Gas*, Sekiyo Gakkaishi **33**(1), 1-12, 1990.

7. K. Klier, R. G. Herman, G. W. Simmons, C. E. Bogdan, J. G. Nunan, and K. J. Smith, *Direct Synthesis of 2-Methyl-1-Propanol/Methanol Fuels and Feedstocks*, in Synthesis Gas Conversion to Liquid Fuels and Upgrading Proceedings - Indirect Liquefaction Contractor's Review Meeting, Vol. I, pp. 258-379, December 1987.

8. J. G. Nunan, C. E. Bogdan, K. Klier, K. J. Smith, C. -W. Young, and R. G. Herman, *Higher Alcohol and Oxygenate Synthesis over Cesium-Doped Cu/ZnO Catalysts*, Journal of Catalysis **116**, pp. 195-221, 1989.

9. J. B. Hendrickson, D. J. Cram and G. S. Hammond, Organic Chemistry, McGraw-Hill Book Company, New York, 1970, Chapter 8.

10. D. J. Cram, Fundamentals of Carbanion Chemistry, Academic Press, New York, 1965, Chapter 1.

11. W. Veda, H. Kurokawa, Y. Moro-Oka and T. Ikawa, *Coupling Reaction Between Methylproprionate and Methanol to Form Methylmethacrylate over Metal Ion-Containing Magnesium Oxide Catalyst*, Chemistry Letters, 819-820, 1985.

12. W. Veda, T. Yokoyama, Y. Moro-Oka and T. Ikawa, Catalytic Synthesis of Vinyl Ketones over Metal Oxide Catalysts using Methanol as the Vinylation Agent, J. Chem. Soc., Chem. Commun., 39-40, 1984.

13. K. Tanabe, M. Misono, Y. Ono and H. Hattori, New Solid Acids and Bases Their Catalytic Properties, Kodansha Ltd., Tokyo, 1989, pp. 333-336.

14. G. H. Unzelman, *Ethers Will Play Larger Role in Octane, Environmental Specs for Gasoline Blends*, Oil & Gas Journal, pp. 44-49, April 17, 1989.

15. Unpublished results, E. L. Weist.

16. G. H. Unzelman, *U. S. Clean Air Act Expands Role for Oxygenates*, Oil & Gas Journal, pp. 44-48, April 15, 1991.

17. Unpublished results, E. L. Weist.

18. Von C. Spindelbalker and A. Schmidt, *Oxygenates as Extenders for Automotive Fuels*, Eerdoel Erdgas 102(10), 1986, 469-474.

FIGURE 1. The dependence of the methanol and C_2-C_6 alcohols rates on gas-hourly space velocity. Reaction conditions: Shell gas, 300°C, 7.0 MPA.

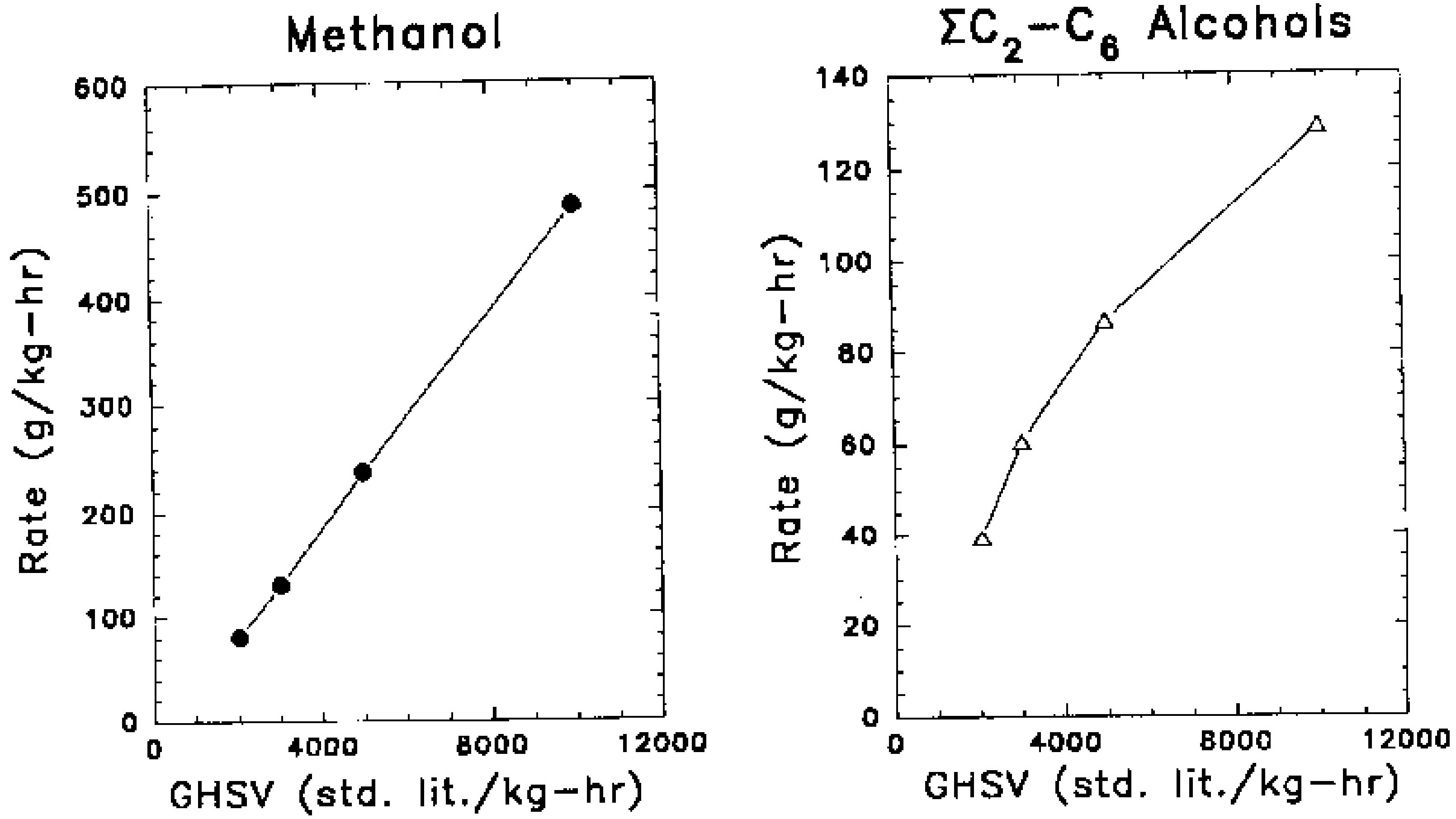


FIGURE 2. The dependence of selectivity on gas-hourly space velocity. Reaction conditions: Shell gas, 300°C, 7.0 MPa.

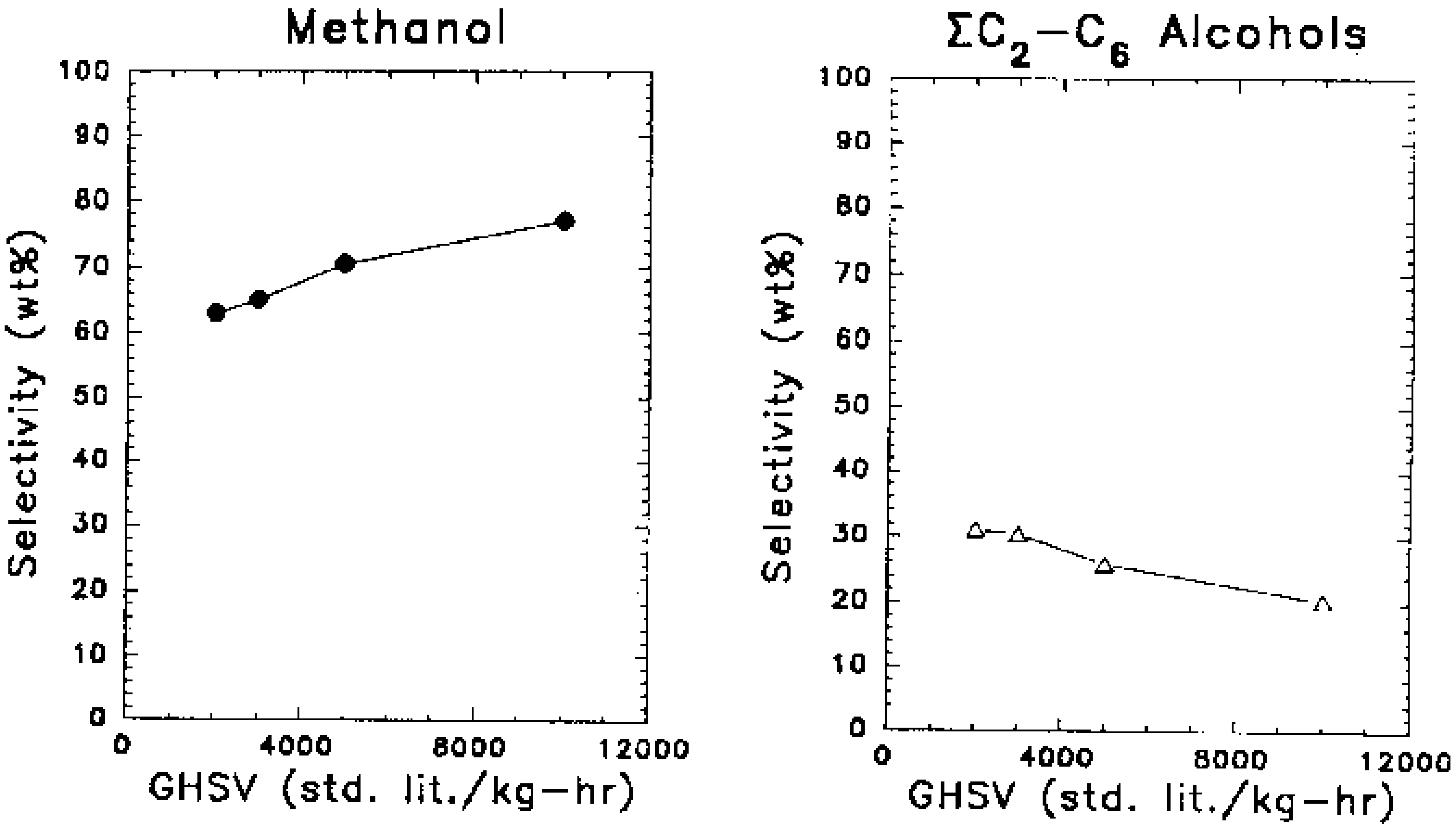


FIGURE 3. Alcohol product distribution.
Reaction conditions: Shell gas, 300°C, 7.0 MPa.

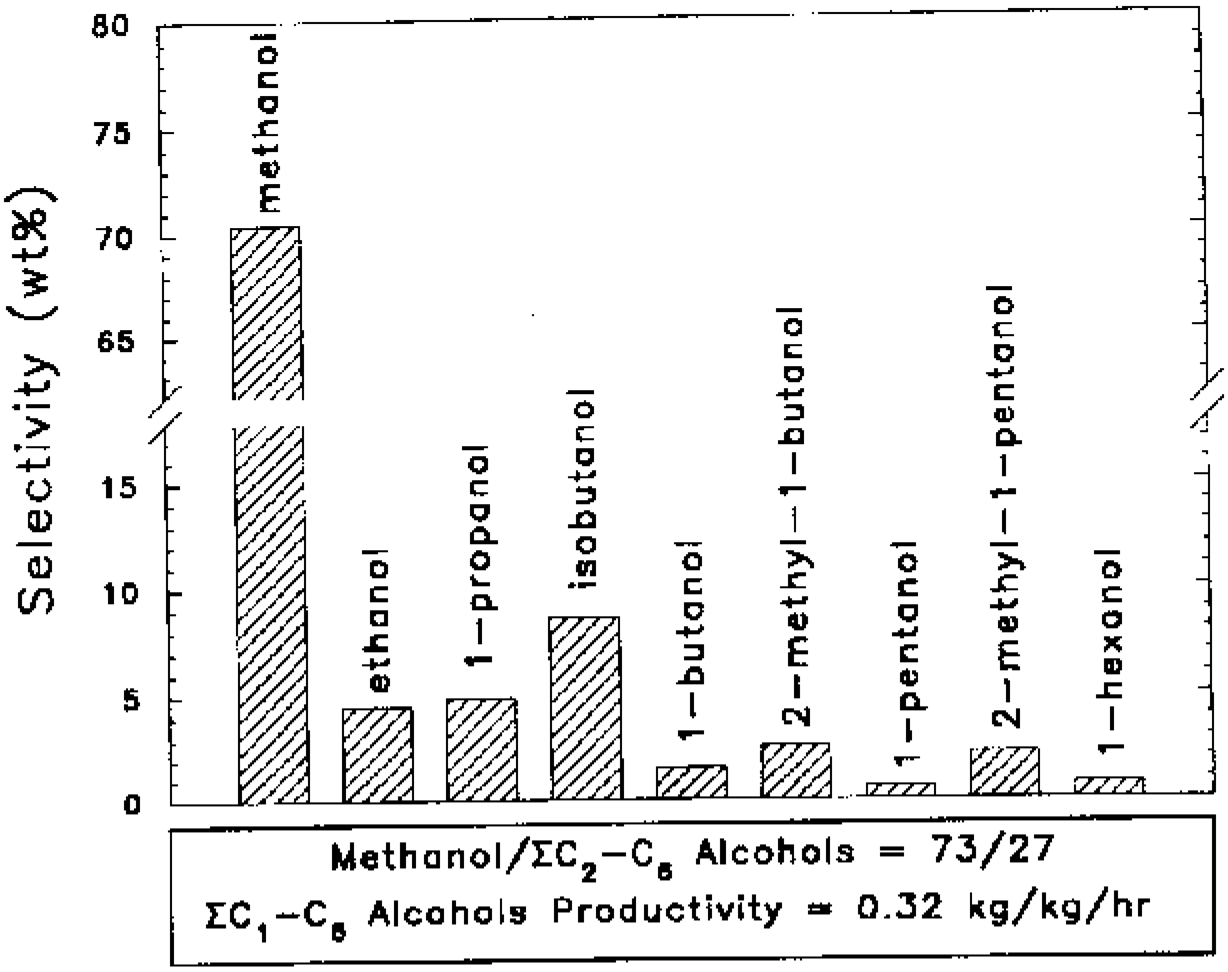


FIGURE 4. The effect of syngas composition on alcohol product rate. Reaction conditions: 300°C, 7.0 MPa.

Texaco Gas: 51% CO, 35% H_2, 13% CO_2, 1% N_2

Shell Gas: 66% CO, 30% H_2, 3% CO_2, 1% N_2

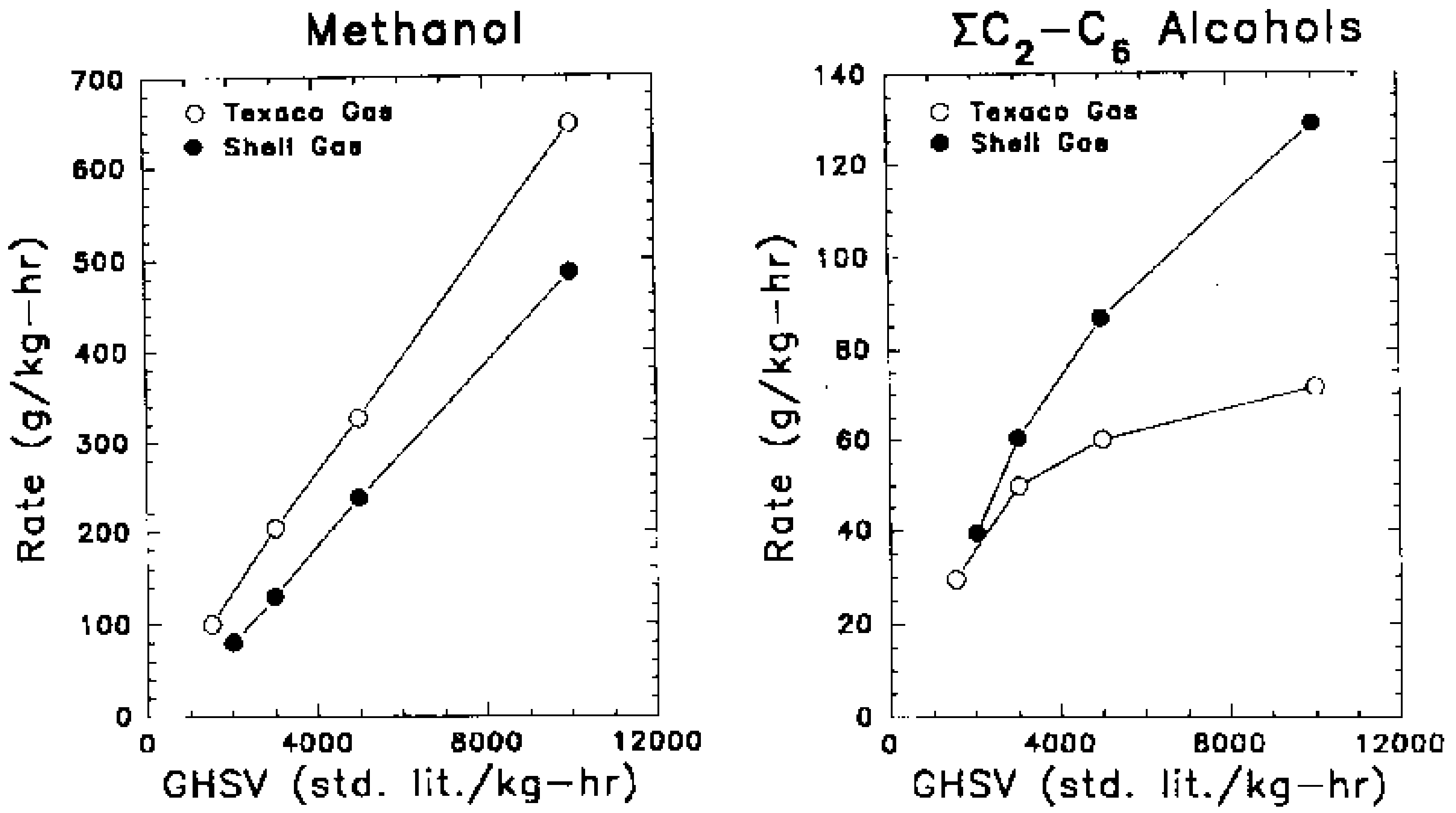


FIGURE 5. The dependence of product selectivity on temperature. Reaction conditions: Shell gas, 7.0 MPa, 5,000 GHSV.

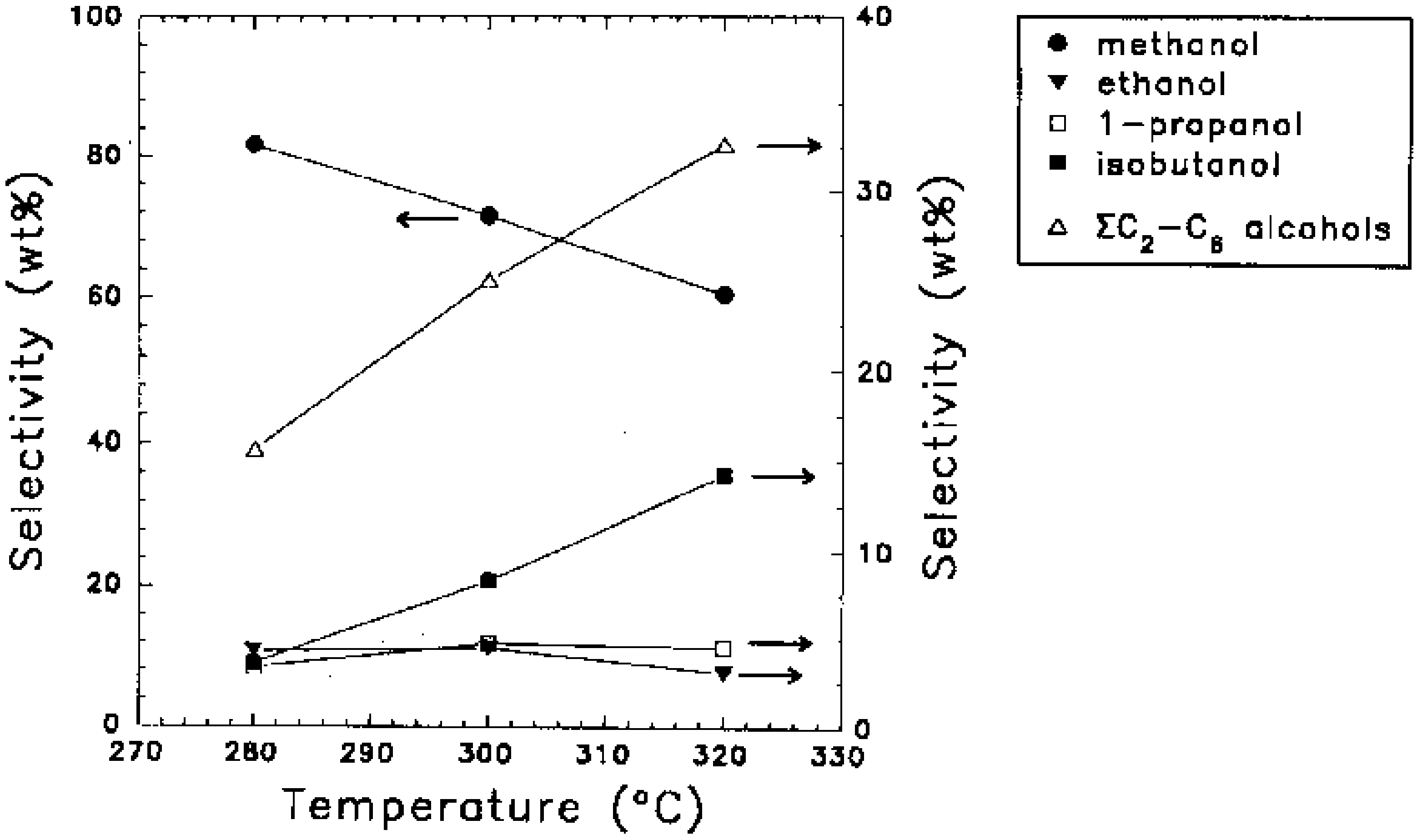


FIGURE 6. Process flow diagram for dual atmospheric gas-phase reactors.