

Higher Alcohol Synthesis From Methanol or Syngas

Lawrence Norcio, Edwin L. Kugler, and Dady B. Dadyburjor

Department of Chemical Engineering

West Virginia University

Morgantown, WV 26506-6102

Introduction

Alcohols are good octane enhancers for gasoline. With stringent restrictions on MTBE use in California, mixed alcohols appear to be the environmentally-friendly fuel additive. Ethanol and methanol have been used as gasoline additives in certain regions of the country for nearly twenty years. However, higher alcohol mixtures (ethanol and those of higher molecular weights) now seem preferable to methanol because of their lower volatility, important for gasoline vapor-pressure specifications.

Prior work in our laboratory has shown that good alcohol synthesis performance can be obtained with molybdenum-based catalysts. The addition of Ni and K to these catalysts improves their performance considerably for higher alcohol synthesis. These catalysts generally need to be reduced prior to reaction. The effects of impregnation order as well as the effects of calcination were also found to be significant. Results from previous study [1] show that the calcined Mo-Ni-K/C catalyst should be a superior higher-alcohol-synthesis catalyst.

The work described in this report focuses on material balance measurements. The emphasis on good material balance data will validate the prior work. The computer-controlled reactor used before has been modified to maximize liquid product collection to aid in the carbon balance measurements.

Methodology

Catalyst Preparation

Activated carbon (20-40 mesh) was obtained from Aldrich. Ammonium heptamolybdate, potassium nitrate, and nickel nitrate, obtained from Fisher Scientific, were used as sources of Mo, K, and Ni, respectively. The incipient-wetness method was used to prepare all samples. Mo was impregnated first followed by Ni and then K. The calcination procedure in flowing nitrogen was carried out after each impregnation step. The calcination temperature varied as follows, 500°C for Mo, 500°C for Ni, and 300°C for K. Typically 0.9 g of catalyst was used for catalyst testing.

Reactivity

Reactivity studies were carried out in a computer-controlled reactor system. Catalysts were reduced in flowing H₂ at atmospheric pressure and 400°C for 12-15 hours prior to use. Higher-alcohol synthesis was studied at 750 psig. The reactor was run isothermally at 250, 300, and 350°C. Gas products were analyzed on-line every two hours using gas chromatography (GC). Liquid products were collected once a day and manually injected to the GC. The GC columns used were HayeSep D_B and DB-Wax.

Summary of Results

A Mo-Ni-K/C catalyst, similar to the one used for previous work [1], was freshly prepared and tested to obtain carbon balance measurements. The catalyst tested contains 18 wt. % Mo, K/Mo=1.2 (molar) and Ni/Mo=0.6 (molar). Small quantities of methane, and traces of

ethane and propane are detected as the gas-phase hydrocarbon products. The liquid product consists of an aqueous phase containing alcohols. Alcohols up to C₅ can be identified with the HayeSep column. No hydrocarbons can be identified in the liquid products.

Figure 1 shows a typical GC chromatograph when a sample of liquid product containing mixed alcohols is injected to the GC. The major components of the mixed alcohols are methanol, ethanol, 1-propanol, and 1-butanol. This result is also observed with the previous work done on a similar catalyst [1].

Table 1 shows the wt.% distribution of water-free mixed alcohols at 250, 300, and 350°C. The amount of condensates (mixed alcohols and water) increases as the reaction temperature increases. The volumes collected over a 24-hour period are 0.35, 1.8, and 4.8 cc at 250, 300, and 350°C, respectively. A similar trend is observed on the %CO conversion and the space-time yield (STY) of higher alcohols. The %CO conversions obtained are 1.97%, 14.63%, and 48.56% while the STY's are 12, 65, and 161 g/h/kg-catalyst, respectively. The calculated selectivity to higher alcohols (wt.% CO₂-free) at T= 350°C is 60% which is the same as the published data [1] for the same catalyst and reaction conditions.

Table 2 shows the summary of the carbon balance calculations at 250, 300, and 350°C. The % accounted carbon at 250, 300, and 350°C are 99.78, 99.38, and 98.71%, respectively.

The liquid product was also injected to another GC with a different column. The column used was SIMDIS-2887, used to analyze high-boiling liquids. Figure 2 shows the GC chromatograph of the alcohol product mixture. Peaks were identified by comparing their retention times with those of alcohol standards. From **Figure 2**, it was found that there are small quantities of alcohols greater than C₅ in the product mixture. It appears that there is a successive addition of a carbon atom forming a homologous series of linear alcohols up to C₂₄. This suggests that methanol also acts as a reactant to form higher alcohols. The implication of this result may become clear as we obtain more data on these higher alcohol products.

Reference

- [1] E. L. Kugler, D. B. Dadyburjor, L. Feng, and X. Li., *Studies in Surface Science and Catalysis*, **130** (2000), 299.

Table 1. The percentage weight distribution of mixed alcohols obtained at various reaction temperatures.

	250°C	300°C	350°C
Alcohol	Wt.%	Wt.%	Wt.%
MeOH	24.82	23.10	18.67
EtOH	42.95	42.66	44.58
2-PrOH	0.89	1.04	1.33
1-PrOH	20.73	20.41	21.37
2-BuOH	0.67	2.15	3.38
2-Me-1-PrOH	1.96	2.03	2.33
1-BuOH	5.39	5.45	5.71
3-Me-1-BuOH	0.81	1.46	0.99
1-PenOH	1.78	1.70	1.66

Table 2. Summary of carbon mass balance for Mo-Ni-K/C catalyst run at various reaction temperatures over a 24-hour period.

	250°C	300°C	350°C
g CO entering	43.35	43.35	43.35
g C from CO entering	18.58	18.58	18.58
g C from CO left	18.21	15.91	10.06
Total g C from hydrocarbons	0.032	0.69	2.31
g C from CO ₂	0.16	1.13	4.20
g C from alcohol	0.14	0.73	1.77
g C accounted	18.54	18.46	18.34
% C accounted	99.78	99.35	98.71

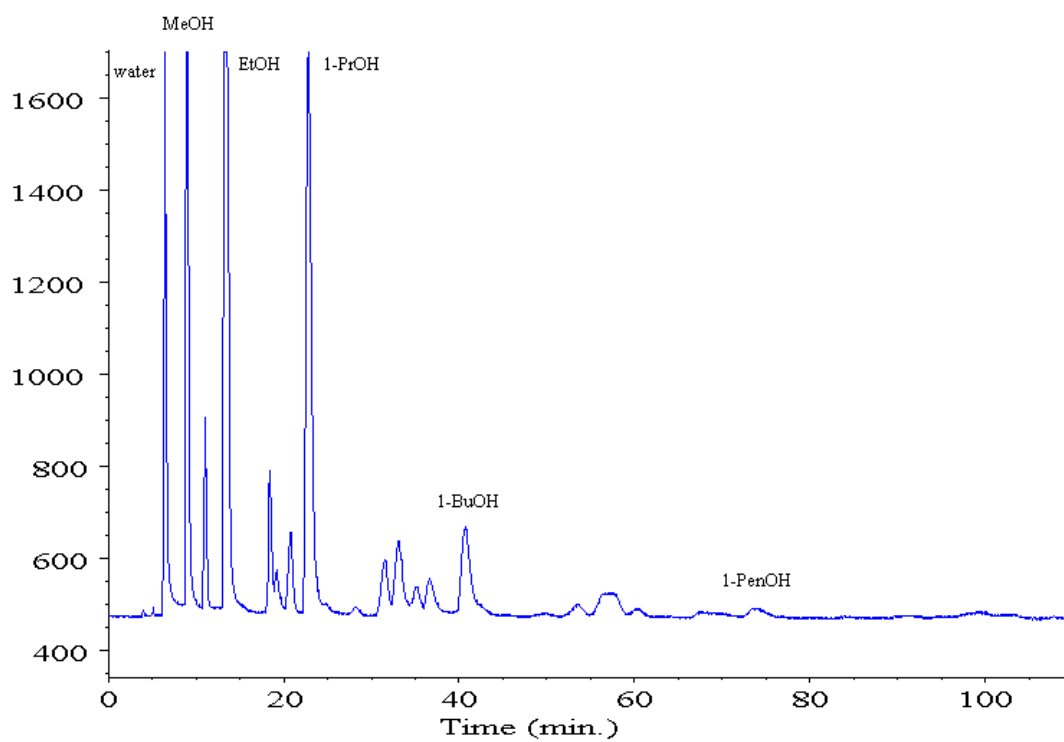


Figure 1. A typical GC chromatograph (TC detector) of mixed alcohols from Mo-Ni-K/C catalyst.

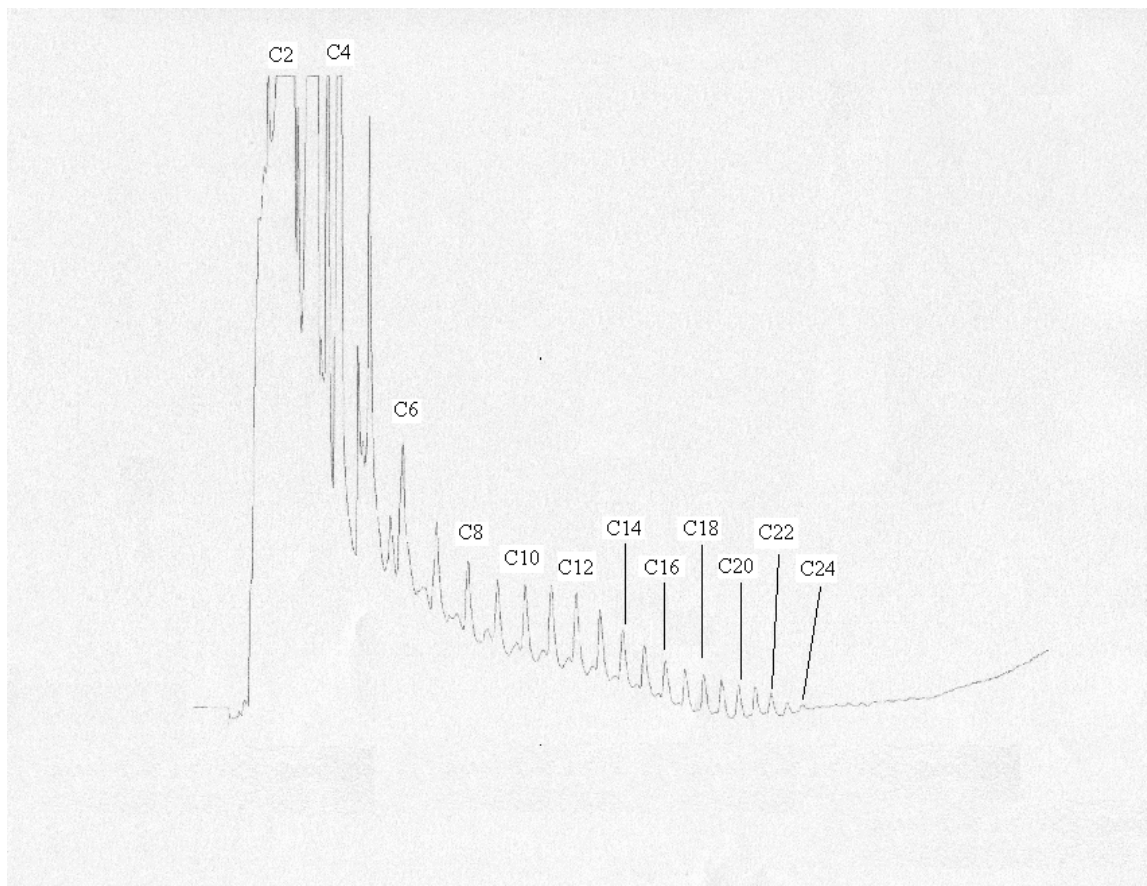


Figure 2. The GC chromatograph of the alcohol product using SIMDIS-2887 column and FI detector.