

PRODUCTION OF MIDDLE DISTILLATES

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ABSTRACT

Existing processes have been assembled in a novel combination capable of producing higher hydrocarbons from natural gas (methane) in high yields. Methane, oxygen, and hydrogen chloride react over an oxyhydrochlorination (OHC) catalyst in a first stage to produce predominantly chloromethanes and water. In a second stage, chloromethane is catalytically converted to higher hydrocarbons, including paraffins, iso-paraffins, naphthenes, olefins, and aromatics, by a shape-selective alumino-silicate zeolite. In the process described, the final hydrocarbon mixture is largely in the gasoline (C₄-C₁₀) boiling range.

The first-stage reaction has been studied under varying conditions of temperature and feed stoichiometry and over a range of residence times. The conversion of reactants, the yields, and product selectivities have been determined over the operating range of the catalyst and reported previously [1-6].

The second-stage reaction has been carried out over a zeolite catalyst with chloromethane as the reactant. Long-term (1,000+ hours) studies have been conducted and the products of chloromethane conversion determined. The products of reaction were similar to those formed when using methanol as a feed.

EXPERIMENTAL

Oligomerization reactions were conducted in a 0.5 inch od x 0.375 inch id (1.27 cm od x 0.95 cm id) x 10 inch (25.4 cm) 304 stainless steel reactor. The inside wall of the reactor was coated with Restek Corporation's Silcocteel® coating. The catalyst was supported in the reactor on a quartz-wool plug and the reactor was operated in an up-flow configuration. A gold-plated thermocouple in the center of the catalyst bed was used to control the temperature of reaction to 350°C ± 0.5. Reactor feeds were controlled by Brooks proportional ratio mass-flow controllers. The feed gas was preheated to approximately 130°C and the products of reaction were heated to approximately 175°C between the exit of the reactor and the cold trap, maintained at -4°C.

The ZSM-5 was obtained from Mobil Oil Corporation. The zeolite was supported on an alumina extrudate and used in the reactor as received. The zeolite accounted for approximately 33% of the total weight of the extrudate.

Prior to each experiment, the catalyst was “burned off” in a stream of 78% helium and 22% oxygen. The pretreatment conditions were to heat the catalyst in the reactor at 350°C for 24 hours, increase the temperature to 450°C and hold for 24 hours, and increase the temperature to 550°C and hold for 72 hours. After, the reactor was purged with helium at reaction temperatures for a minimum of 1 hour before the introduction of the chloromethane.

Products of reaction were directly sampled and analyzed by an online dual-column gas chromatograph (GC). The GC, a Hewlett-Packard 5890 Series II, was equipped with a 100 m X 0.25 mm i.d. fused silica column coated with 0.5 μm film of 100% dimethylpolysiloxane (Petrocol DH obtained from Supelco) and a 50 m X 0.32 mm porous layer open tubular (PLOT) column containing $\text{Al}_2\text{O}_3/\text{KCl}$ (obtained from Chrompack). The GC was temperature programmed at 1°C/minute from 30°C to 200°C. Helium was used as the carrier gas having an average linear velocity, at 30°C, of 41 mL/minute for the Petrocol column and 32 mL/minute for the PLOT column. The Petrocol column was used to separate the liquid components of reaction while the PLOT column was used to separate the gaseous components. Dual flame ionization detectors (FID's) were employed to detect the separated components.

RESULTS

Conversion of methane to chloromethane

The conversion of methane to chloromethane by the oxyhydrochlorination (OHC) reaction has been extensively studied and reported previously [1-6]. The process has been determined to be technically feasible.

Conversion of chloromethane to transportation fuels

Conversion of chloromethane over ZSM-5 to gasoline-range hydrocarbons has been observed to occur under conditions identical to those for the conversion of methanol. Conversions of chloromethane at the various space velocities as a function of time on stream is shown in Figure 1. Conversions at all three space velocities are high (>98% after 1,000 hours on stream). The two lower space velocities (WHSV = 0.34 hr^{-1} and 1.00 hr^{-1}) exhibit the highest conversions (>99.7%).

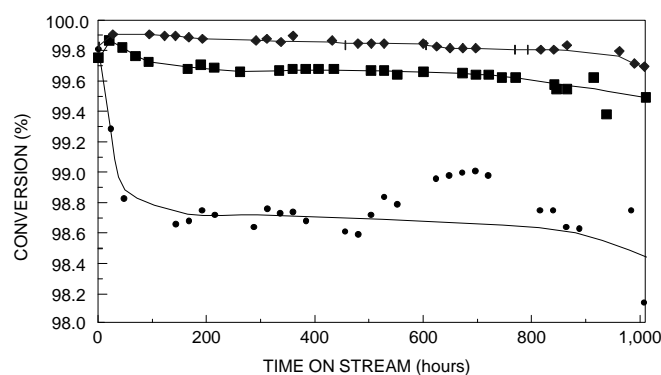


FIGURE 1. Chloromethane conversion as a function of time on stream. Reaction conditions: Temperature = 350°C. \blacklozenge) \blacklozenge) WHSV = 0.34 hr^{-1} , \blacksquare) \blacksquare) WHSV = 1.00 hr^{-1} , \bullet) \bullet) WHSV = 3.00 hr^{-1} . Data from Petrocol column on GC.

The gas chromatograms of the products from chloromethane oligomerization over ZSM-5 at the start and end of the run are shown in Figure 2. Over 300 compounds were identified in the product stream. The identity of the major components in the product streams and their approximate weight percent are available upon request.

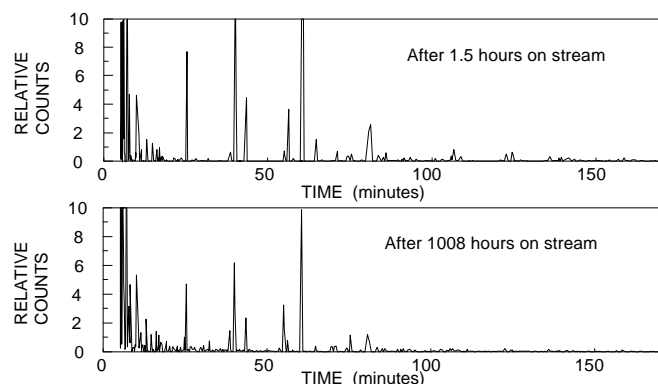


Figure 2. Gas Chromatograms of the Product from Chloromethane Conversion over ZSM-5.

The changes in product distribution as time on stream increases is consistent with the progressive coking of the zeolite over time[7].

Several trends are apparent from the GC data. Product distribution is dependent on both the space velocity and the time on stream. Independent of space velocity, as time on stream increases the amount of paraffin, iso-paraffin, and aromatic compounds decrease. A corresponding increase in the amount of olefins is observed with increasing time on stream. The production of naphthenes remains relatively constant with time on stream. The largest change in product distribution occurs during the first 200 hours of reaction. After this the product distribution begins to

line out. Increasing the space velocity results in a decrease in the amount of paraffins, iso-paraffins, aromatics, and naphthenes produced. The production of olefins increases with increasing space velocity.

Comparison of product yield for the conversion of chloromethane with that reported in the literature [7] for conversion of methanol is shown in Figure 3. The trends for the two reactants are similar. Methanol produces slightly more iso-paraffins, where chloromethane produces slightly more aromatics and C₃ - C₅ n-paraffins.

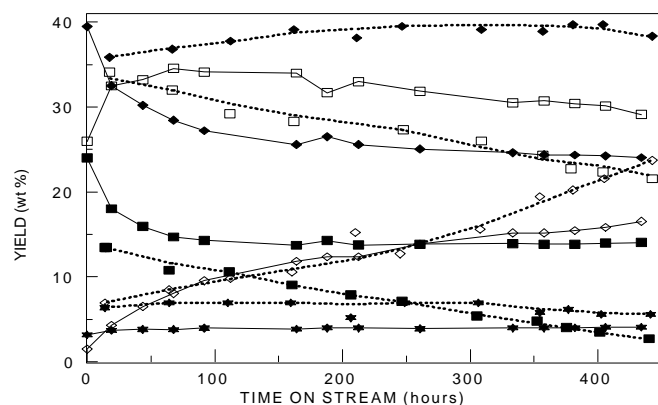


FIGURE 3. Comparison of product yield for the conversion of methanol and chloromethane over ZSM-5. Mobil data for methanol at WHSV = 1.6 hr⁻¹,)))) this paper's data for chloromethane at WHSV = 1.00 hr⁻¹, (◆)) ◆ iso-paraffins, (■)) ■ C₃ - C₅ N-paraffins, (□)) □ aromatics, (◇)) ◇ olefins, (*)*) * naphthenes. Mobil data from Reference 7, page 85.

Figure 4 shows the carbon number yield as a function of time on stream for the 1,000+ hour run at WHSV of 1.00 hr⁻¹. The data shows a bimodal distribution of products, with maxima at C₄ and C₉. A similar bimodal product distribution is observed for experiments conducted at the other space velocities.

It appears at first sight that the majority of products from chloromethane oligomerization are light hydrocarbons (C₁- C₄). As shown in Figure 5, approximately 60 weight percent of the total product is C₅ or higher. Methane and ethane, the two most stable and least desirable hydrocarbon products, account for less than 2 weight percent of the total product. The remainder of light hydrocarbon products,

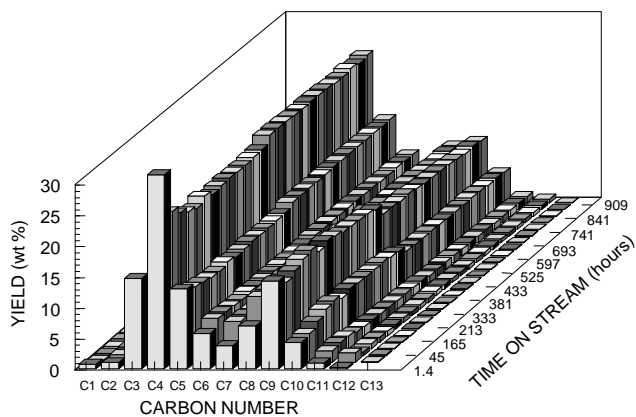


FIGURE 4. Carbon yield as a function of time on stream. Reaction conditions: Temperature = 350°C, chloromethane WHSV = 1.00 hr⁻¹

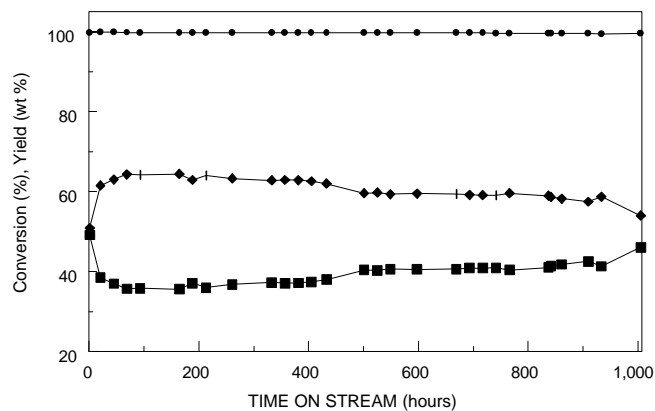


Figure 5. Conversion and product yield for the reaction of CH₃Cl over ZSM-5 at 350°C and WHSV = 1 hr⁻¹. CH₃Cl Conversion ●—●, C₁-C₄ yield ■—■, C₅+ yield ◆—◆.

accounting for approximately 38 weight percent, could be further upgraded to transportation fuels, increasing the total liquid product.

The majority of compounds C₆ and higher are aromatic consisting mainly of methyl-substituted benzenes. Table I shows the normalized aromatic product distribution for chloromethane conversion over ZSM-5. For comparison, the calculated thermodynamic equilibrium data for methanol oligomerization [8] and the literature data for methanol conversion over ZSM-5 [9] are listed. The distribution for the dimethylbenzenes from methanol and chloromethane at WHSV of 0.34 hr⁻¹ and 1.00 hr⁻¹ are close to the calculated thermodynamic equilibrium values.

The dimethylbenzene distribution for chloromethane at WHSV of 3.00 hr⁻¹ deviates from the equilibrium values producing more of the 1,2 and 1,3 isomer. We attribute this deviation from the thermodynamic equilibrium values to our reactor configuration. At the high space velocities, the contact time in the catalyst bed is short. The short contact time does not allow the 1,2- and 1,3-dimethylbenzene enough time in the catalyst “cage” to isomerize to the thermodynamically favorable 1,4-isomer.

The higher substituted benzenes, trimethyl- and tetramethylbenzenes, show large deviations from thermodynamic equilibrium values when chloromethane is the feed. This trend was also observed by Chang [9] when methanol was the feed, however, the deviation from equilibrium values is greater for chloromethane-derived products. The deviation from equilibrium for the higher substituted benzenes has been attributed to the zeolite’s “shape-selectivity” [9].

Trace amounts (<0.1 wt.%) of 2-chloropropane and 2-chlorobutane were also found in the products from chloromethane oligomerization. We hypothesize that these compounds had been formed by vapor phase addition of hydrogen chloride to propene and butene, all products of chloromethane oligomerization. This type of addition has been reported to occur under similar reaction conditions [10]. It was further proposed that if these chlorinated alkanes came in contact with the zeolite catalyst, they would be oligomerized. To test the latter, several primary, secondary, and tertiary chlorocompounds of propane, butane, and pentane

were allowed to react over ZSM-5 under the conditions for chloromethane oligomerization. In each case, the halocarbon was converted to aromatic hydrocarbons and hydrogen chloride, confirming our hypothesis.

CONCLUSIONS

Methane can be converted into higher hydrocarbons boiling in the gasoline range by the two-stage process described. We have shown that methane, hydrogen chloride, and oxygen can be reacted over a supported copper chloride catalyst to produce chloromethane with high yield and selectivity.

The oligomerization of chloromethane to gasoline-boiling-range hydrocarbons occurs under conditions identical to those for methanol. Dry hydrogen chloride, the by-product of oligomerization, is recoverable from the product stream and may be recycled for use in the OHC step. Long-term exposure of the zeolite to hydrogen chloride and multiple regenerations do not appear to affect either conversions or product distribution.

TABLE I. Normalized Aromatic Product Distribution for Conversions Over ZSM-5

COMPONENT	Equilibrium Distribution [8]	Methanol LHSV = 1.0 hr ⁻¹ [9]	Chloromethane WHSV = 0.34 hr ⁻¹	Chloromethane WHSV = 1.00 hr ⁻¹	Chloromethane WHSV = 3.00 hr ⁻¹
	377°C	371°C	350°C	350°C	350°C
Benzene	40.1	13.0	9.4	22.9	44.8
Methylbenzene	57.8	81.0	70.8	55.2	38.7
Ethylbenzene	2.0	6.0	19.8	21.9	16.5
1,2-Dimethylbenzene	23.7	21.5	21.7	19.3	29.6
1,3-Dimethylbenzene	52.7	54.6	55.8	56.9	62.1
1,4-Dimethylbenzene	23.6	23.9	22.5	23.8	8.3
1,2,3-Trimethylbenzene	7.9	6.4	3.4	3.6	5.2
1,2,4-Trimethylbenzene	66.1	78.7	89.0	90.3	85.3
1,3,5-Trimethylbenzene	26.0	14.9	7.5	6.1	9.5
1-Ethyl-2-methylbenzene	17.4	14.6	4.6	1.6	2.0
m + p ethyl-methylbenzene	82.6	85.4	95.4	98.4	98.0
1,2,3,4-Tetramethylbenzene	20.2	9.3	10.1	11.9	13.5
1,2,3,5-Tetramethylbenzene	38.4	44.2	34.3	30.9	33.0
1,2,4,5-Tetramethylbenzene	41.4	46.5	55.7	57.2	53.4

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DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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