

ISOBUTYLENE SYNTHESIS FROM HYDROGEN LEAN SYNGAS IN SLURRY AND TRICKLE BED REACTORS

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INTRODUCTION

Due to environmental regulations, new gasoline formulations will be introduced to the market in the coming decade to reduce automobile exhaust emissions of CO, nitrous oxides and photoreactive unburned hydrocarbons. Addition of oxygenates such as methyl tertiary butyl ether (MTBE) to new formulations is necessary to maintain an acceptable octane number required for modern automobiles. The production of MTBE is currently limited by the supply of isobutylene. We and other groups have recently reported data on selective formation of isobutylene from hydrogen lean synthesis gas (isosynthesis) in fixed beds over catalysts based on zirconia in the temperature range 573-723 K and the pressure range 0.5 - 100 atm. All the studies in the literature on isosynthesis have been conducted in gas-solid fixed bed reactors. Using a three phase gas-oil-catalyst slurry or trickle bed reactor for isosynthesis can have certain advantages. Continuous circulation of the oil phase may enable separation of light components from the heavy components (C_3+ which are produced by the reaction) at the gas oil separator. The heavy components can be circulated back to the reactor dissolved in the oil and further converted into light hydrocarbons. The CO/H_2 ratio in the oil phase may also be quite different than the CO/H_2 ratio in the feed gas due to the differences in Henry's Law Constants for hydrogen and carbon monoxide which may affect the product distribution. The reaction can be run in the absence of mass transfer limitations in a slurry reactor. There is evidence in the literature that isosynthesis reactions become controlled by external mass transfer at temperatures above 723 K. Other advantages for the slurry reactor include better temperature control and low capital costs, as opposed to fixed bed reactors. In this study, we report the results of experiments on isosynthesis conducted in a laboratory scale slurry reactor and a trickle bed reactor.

EXPERIMENTAL

A schematic diagram of the trickle bed and slurry reactor system is shown in Figure 1. The feed gases are purified by flow through a guard bed consisting of activated carbon and molecular sieves with particle size of 0.16 cm. Hydrogen and carbon monoxide flowrates are controlled with Brooks model 5850E mass flow meters which have flow ranges of 0-2 and 0-1.5 standard liters per hour, respectively. The flow meters were calibrated by checking the controller set point versus the volumetric flowrate determined by the bubble meter. The feed gas streams are combined at a predetermined CO/H_2 ratio. To enhance mixing, the gases are passed through a bed of glass beads prior to the reactor. Decalin was fed to the unit using a Milton Roy pump. A relief valve, which is set at 106 atm, was placed before the reactor to prevent uncontrolled pressure rises in the system.

The trickle bed reactor is a 316 stainless steel tube, 25 cm long, 0.96 cm ID, and 1.2 cm OD. It was mounted vertically in a bed of aluminum pellets. The reactor is divided into three sections. Prior to and after the 7 cm catalyst bed are 6 and 12 cm supporting sections filled with 0.2 cm diameter glass beads. The reactor was heated by the heating block and controlled by a Omega model 6100 temperature controller. A thermocouple inserted through the middle of the catalyst bed was used to measure the temperature of the bed.

The slurry reactor was a stirred 100 cm³ Autoclave model EZ seal with six ports and one thermowell. The feed was introduced to the bottom of the reactor through a dip tube. A 50 micron porous metal filter was connected to the effluent port to prevent the entrainment of catalyst particles. A baffle bar and impeller were connected to the stainless steel reactor cover. The impeller was driven by a Magnadrive II stirrer. Cooling water was passed through the Magnadrive assembly to keep the temperature of the assembly in the permissible range. The reactor was heated using a furnace supplied by the manufacturer which was controlled by a Thermolyne Furnatrol I furnace controller.

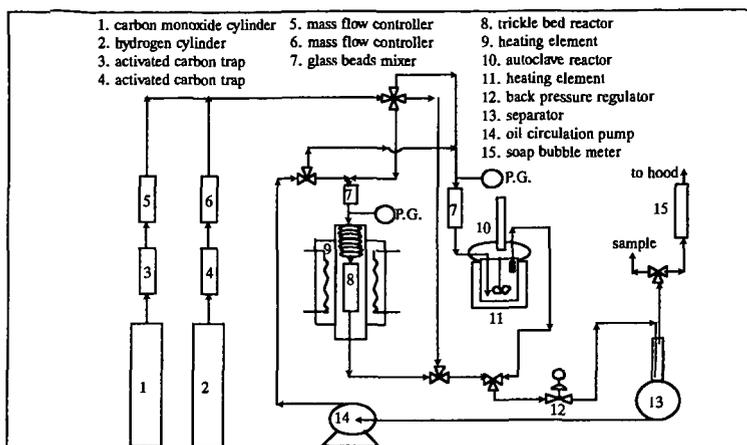


Figure 1. Schematic diagram of the experimental set-up

The reactor pressure was maintained with a Grove model 91W back pressure regulator. The reactor effluent passed through the back pressure regulator where the pressure was reduced to atmospheric pressure prior to the gas oil separator. The decalin collected at the bottom of the separator was recycled to the reactor. After the gas oil separator a sampling port was used to take gas samples for analysis. The effluent gas was passed through a soap bubble meter to measure the volumetric flow rate before it was vented to a fume hood. The decalin used in this study was obtained from Sigma Chemical and exists as *cis* and *trans* isomers of decahydronaphthalene with a minimum purity of 98 % as determined by gas chromatography.

RESULTS AND DISCUSSION

Slurry reactor

Zirconia was synthesized in the laboratory by precipitation. It had a surface area of 92 m²/g. Figure 2 shows a comparison of the hydrocarbon product distributions for the slurry and fixed bed reactors. The comparisons have been made at similar space velocities and similar conversions. Although the CO conversion is lower for the slurry reactor at a fixed space velocity, the selectivities to light hydrocarbon products are higher at equal conversions, and less C₅+ products are produced. This is due the fact that some of the heavier C₅+ products formed during the reaction are circulated back to the reactor in the oil and further crack to lighter hydrocarbons. The lower CO conversion for the slurry reactor at equal space velocity can be entirely accounted by lower performance of a CSTR as opposed to a PFR. As seen in Figure 3, changes were observed in the distribution of C₄ products. Figure 4 shows the comparison of product distribution for different CO/H₂ ratios.

The mass transfer resistances were calculated based on the data. Gas bubble to liquid mass transfer coefficients were calculated using the Calderbank and Moo-Young correlation and liquid to particle mass transfer coefficients were calculated using various correlations in the literature. These resistances were found to be negligible. The effectiveness factors were found to be very close to unity. Therefore, it is believed that the reactions were run in the kinetically controlled regime in the absence of any mass transfer limitations.

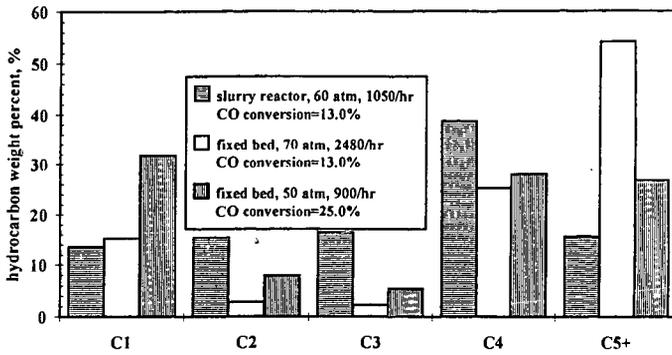


Figure 2. Hydrocarbon product distributions in fixed bed and slurry reactors at 400 °C.

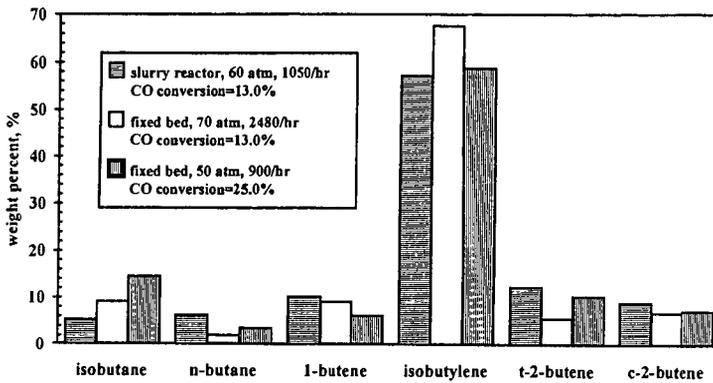


Figure 3. C₄+ product distributions in fixed bed and slurry reactors at 400 °C.

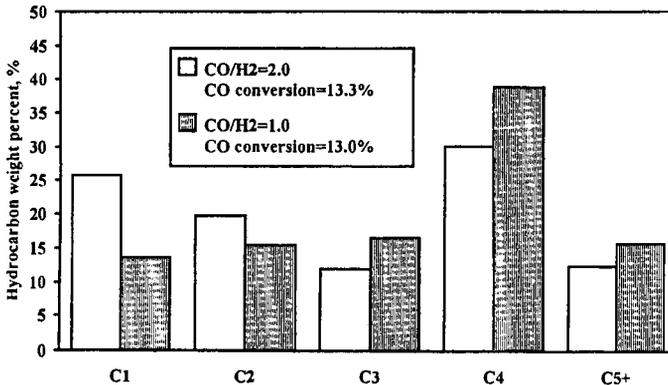


Figure 4. Effect of CO/H₂ ratio on hydrocarbon product distribution at 400 °C.

Trickle bed reactor:

Experiments using the trickle bed reactor were conducted with commercial zirconia with a surface area of 52 m²/g. A comparison of the performance of the catalyst when operating the reactor in the fixed and trickle bed modes at 669 K and 51 atm is shown in Figures 5 and 6. The selectivity for isobutylene and the C₄ components was higher when operating the reactor as a conventional gas phase fixed bed reactor than when operating the reactor as a trickle bed. The CO conversion was approximately the same for both modes of operation. The product distribution obtained with the trickle bed contains more C₃'s, C₄'s and methane and less C₅+ than the product distribution obtained when operating in the gas phase fixed bed reactor mode. A greater amount of propylene is produced in the trickle bed than with the fixed bed gas phase reactor. As shown in Figure 7, oil flow rates were shown to have minor effects on the product distribution. Figure 8 shows that as oil flow rate increases, a slight decrease in CO conversion is observed. This may be due to the decrease of the residence time of the gas through the reactor.

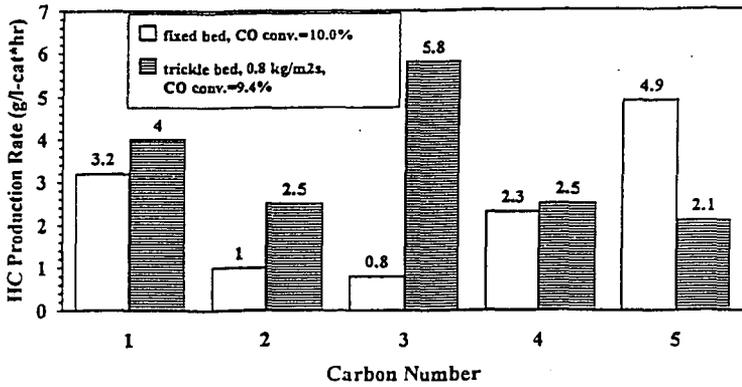


Figure 5. Comparison of hydrocarbon product distribution for fixed and trickle bed reactors at 669 K, 51 atm, 1/1 CO/H₂ ratio and 89 seconds space time.

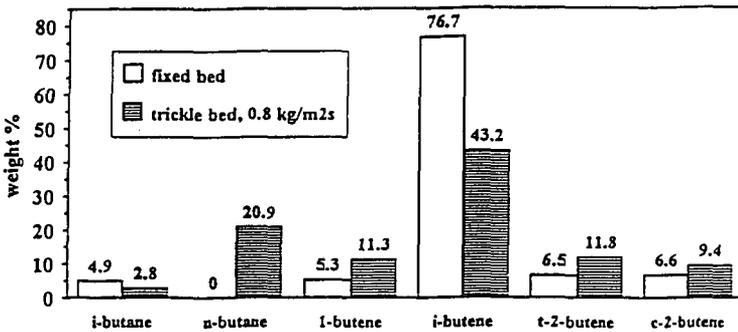


Figure 6. Comparison of C₄ distribution for fixed and trickle bed reactors at 669 K, 51 atm, 1/1 CO/H₂ ratio and 89 seconds space time.

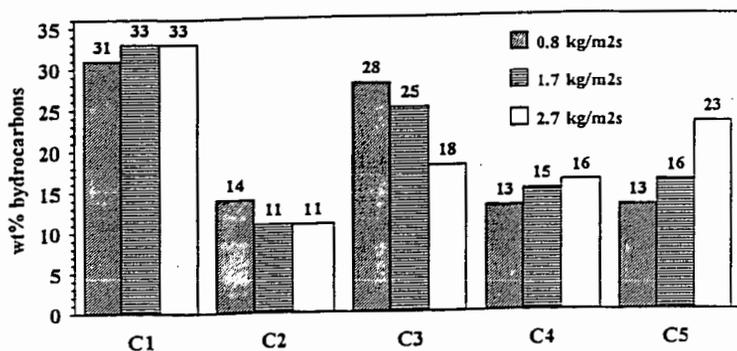


Figure 7. Change in hydrocarbon distribution with oil flowrate at 669 K, 51 atm, 1/1 CO/H₂ ratio and 668 (1/hr) space velocity.

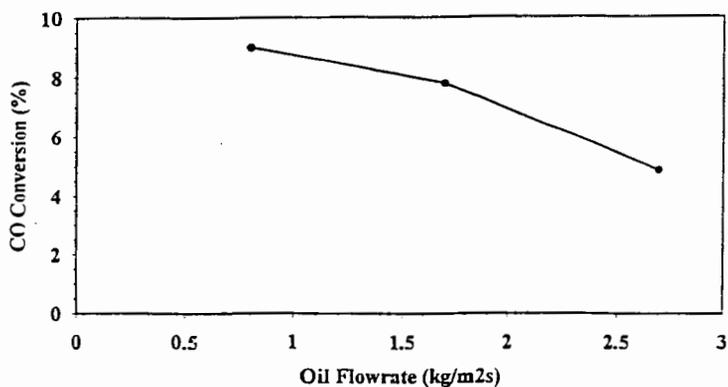


Figure 8. Variation of CO conversion with oil flow rate in the trickle bed reactor at 669 K, 51 atm, 1/1 CO/H₂ ratio and 668 (1/hr) space velocity.