

# The Effect of 1-Butanol Co-Feeding on Propylene Production in the MTP Reaction

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## Abstract

The propylene production with 1-butanol co-feeding for methanol in relation to propylene process (MTP) at 440-490 °C temperature range and at 0.9-15 hr<sup>-1</sup> WHSV range over H-ZSM-5 zeolite catalyst is assessed in a isothermal fixed-bed reactor. The feedings here are of: pure 1-butanol, pure methanol and a 1-butanol and methanol mixture. The effect of 1-butanol co-feeding on selectivity of propylene is assessed through RSM an experimental design method. The results indicate that the selectivity of propylene is 69% in the feed mixture of 13, 37 and 50 wt% of 1-butanol, methanol and water, respectively. The optimum conditions to obtain high level of propylene selectivity is suggested to be at 480 °C, WHSV of 0.9 hr<sup>-1</sup> and 1-butanol concentration of 0.135 wt.% through RSM method. The sensitivity analysis of the RSM method reveals that the WHSV is the most effective parameter on the propylene selectivity with a P-value of 0.003.

## Keywords

MTP Process, Selectivity, Co-Feeding, H-ZSM-5 Catalyst, RSM

## 1. Introduction

Due to an increase in global demand for polypropylene and the price, of oil the FCC and steam cracking processes which are the major contributors in propylene production and other light olefins worldwide cannot supply this demand. Therefore, applying alternative routes for production light olefins has gained importance. In this context, the methanol to hydrocarbon process (MTH), which was discovered accidentally, has been suggested, followed by discovery of methanol to olefins (MTO) and methanol to propylene (MTP) processes (Plotkin, 2005).

The MTP reactions can take place over the acidic zeolite catalysts above 460 °C. Aluminosilicate zeolith (H-ZSM-5) is a commonly consumed catalyst in MTP process. In today practice the MTP process is more popular than the MTO, since the demand on propylene is more than ethylene (Plotkin,

2005). Unlike MTO process which is based on the silicoaluminophosphate catalyst (SAPO-34), MTP process is based on the high Si/Al ratio (up to 200) aluminosilicate zeolite (Liu et al., 2009). This catalyst noticeably increases the propylene production with a reasonable resistance against coke formation.

Zhao et al. (2006) ran direct synthesis of propylene and light olefins from dimethyl Ether. Where, propylene was produced with a selectivity of 45% by direct conversion of dimethyl ether over the ZrO<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub> modified H-ZSM-5 catalyst at atmospheric pressure. The ratio of propylene to ethylene was 16 (Zhao et al., 2006).

Dreyer et al. (2010) assessed the possibility of enhancement of olefin production through renewable aliphatic feedstocks and co-feed lignin derivatives by applying experimental surrogates by a millisecond catalyst bed. Their results indicate that under the optimal

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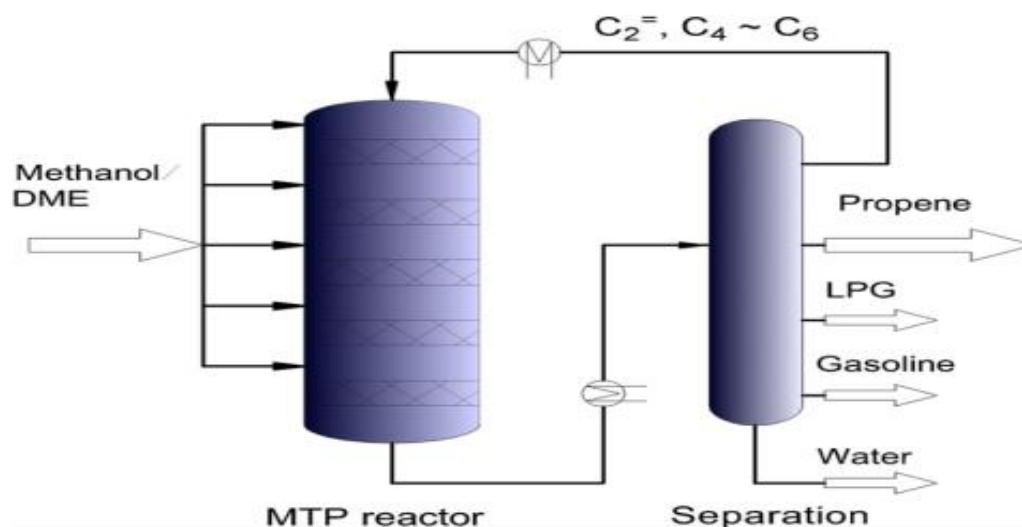
conditions, selectivity of pure *n*-hexane towards ethylene and propylene is increased from ~35% to ~65% when molar mixture of benzene and *n*-hexane is consumed at 50:50 (Dreyer et al., 2010).

Li et al assessed the co-reaction of ethylene and methanol in a modified H-ZSM-5 catalyst. Their results indicate that the co-feeding of ethylene and methanol yields a considerable conversion of both reactants. Meanwhile, high propene selectivity (ca. 80%) is obtained at lower conversions (Li et al., 2008). Bleken et al followed the strategy of increasing the propene selectivity over ZSM-5 catalyst by applying four modified catalysts and revealed that the desired propylene to ethylene ratios (>5) with 35% propylene selectivity are obtained in the fluoride-based catalysts (Bleken et al., 2012). Gong et al. illustrated that by coupling conversion of methanol and  $C_4$  hydrocarbons, a comparatively high propylene yield of 46.0 wt. % is obtained on La/HZSM-5 catalyst (Gong et al., 2012). Jiang et al proved that by recycling a portion of the

MTP products, a 40% propylene yield is guaranteed through a single reactor where simulation predictions indicate that it is possible to achieve higher production yields of (~70%) provided a two-stage fixed-bed reactor system is applied (Jiang et al., 2014).

As to the MTP process with multiple-stage adiabatic fixed bed reactors, originally developed by Lurgi, Company (Bach et al., 2004; Birke et al., 2011; Koempel and Liebner, 2007), Fig. 1, all alkenes other than propene are recycled back into the reactor inlet in order to increase the propene selectivity up to 60%.

From the previous works, it is revealed that the recycled stream has a positive effect on propylene selectivity due to presence of high alkenes like  $C_4$ ,  $C_5$  and  $C_6$ . Hence, in this study, the effect of 1-butanol co-feeding, as a precursor for instantaneous production of  $C_4$  alkenes in the H-ZSM-5 catalysts, on propylene selectivity and yield are examined through the RMS design of experiment technique.



**Figure 1.** Schematic Diagram of MTP Process.  
(Bach et al., 2004; Birke et al., 2006; Koempel and Liebner, 2007)

## 2. Experimental

### 2.1. Setup and Catalyst

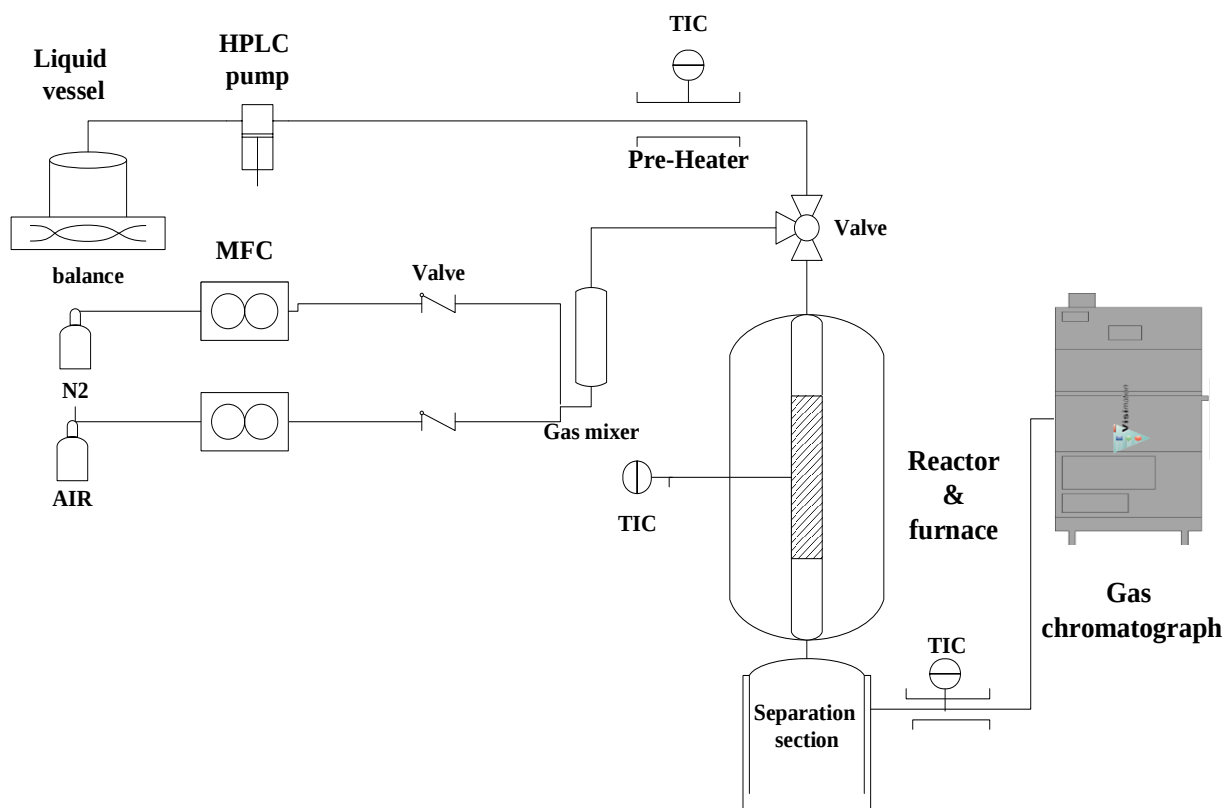
The H-ZSM-5 catalyst prepared by Süd-Chemie Company is applied in this study. This catalyst has the Si/Al ratio of 200, with a 5 mm height, and of 2 mm diameter. The schematic of the experimental setup is shown in scheme 1. The fixed-bed reactor is a piece of 1.2 cm inner diameter stainless steel tubing with 60 cm length mounted vertically on a cubic furnace. The runs are carried out under atmospheric pressure in an automated reaction apparatus. The feed is pumped into the pre-heater and vaporized before entering the reactor; the feed temperature is kept close to the reaction temperature. The reaction mixture after passing through the catalyst bed is converted to product species ready to be sent to gas chromatography for analysis.

The catalyst is loaded into the half bottom of the PFR and held in place with quartz wool. A stainless

steel wire mesh is inserted into half of the reactor to hold the catalyst in place and keep the catalyst and quartz beads separated.

A K-type thermocouple (with indicator HANYANG NUX-PX9) is inserted into the catalyst bed through the half bottom of the PFR. In order to set the WHSV to the appropriate values, the methanol flow rate (with purity of >99.99) and 1-butanol (from Merck KGaA) are controlled with HPLC pump (Eldex-PN: 5982 optos 35M).

Before each test, the catalyst is heated up to 480 °C first, next, then steaming of the fresh catalyst begins and then catalyst bed is exposed to a constant flow of nitrogen (~35 mL/min). The feed and products are analyzed through VARIAN-CP 3800 gas chromatography equipped with flame ionization detector (FID, 220 °C), HP-PLOT/Q capillary column (30 m × 0.32 mm × 32 µm,) and CP-SIL 5CB(30 m × 0.32 mm × 0.25 µm).



Scheme 1. Schematic Diagram of Catalytic Reaction System

## 2.2. Theory/ Calculation

The reactant conversion and product selectivity are evaluated under 95% mass balance accuracy through the following formula or equations:

$$\text{1-butanol conversion} = \frac{F_{b,input} - F_{b,out}}{F_{b,input}}$$

$$\text{methanol conversion} = \frac{F_{M,input} - F_{M,out}}{F_{M,in}}$$

$$\text{products selectivity} = \frac{F_i}{\sum_{i=1}^p F_i}$$

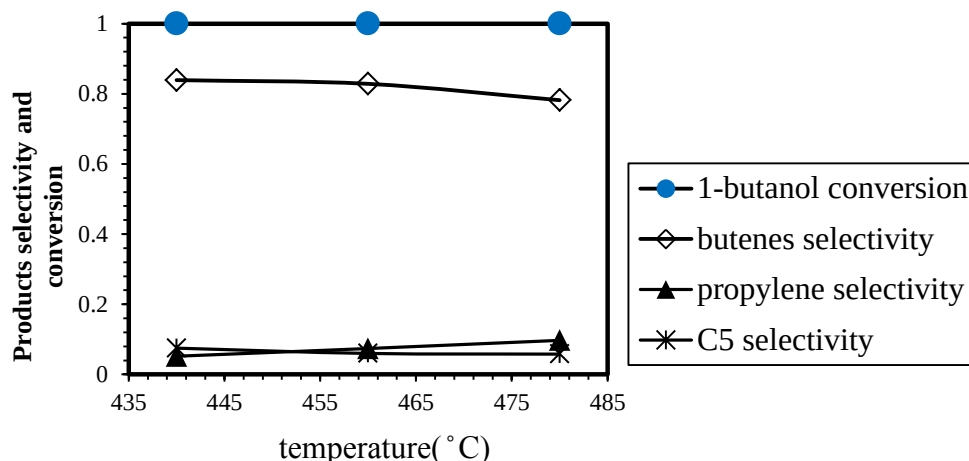
In the last formula,  $F_i$  is the flow rate of  $i^{th}$  product species, subject to reaction conditions, 1-butanol is almost completely converted on the catalyst, while, the level of methanol conversion depends on the reaction conditions.

## 3. Results and Discussion

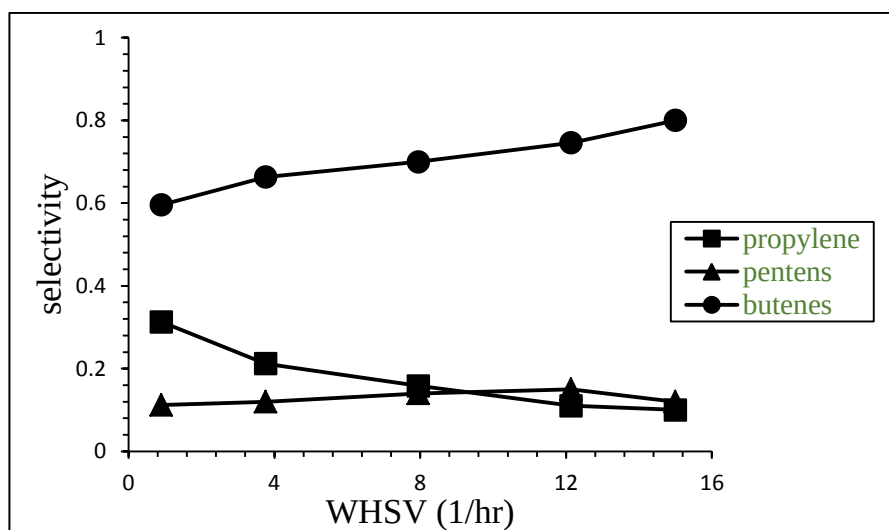
In this article, the effect of 1-butanol co-feeding on propylene production in the MTP reactions is assessed. The reaction of pure 1-butanol is conducted to evaluate the level of 1-butanol conversion first, next, and the relevant product selectivity; the maximum value of  $C_4$  olefins is desired. And finally, the product distribution of methanol with and without the Co-feed species is analyzed.

### 3.1. Reaction of Pure 1-Butanol

Conversion of 1-butanol over H-ZSM-5 is performed at 440 °C, 460 °C and 480 °C in the fixed-bed reactor. The products selectivity and conversion of 1-butanol are shown in Figs. 2 and 3 as a function of temperature and space velocity, respectively. As observed in Fig 2, the 1-butanol conversion is completed over the entire range of the considered temperature.



**Figure 2.** Effect of Temperature on Conversion of 1-Butanol and Selectivity of Butanes, Propylene and Pentens using the Pure 1-Butanol Feed (WHSV = 40 1/hr).



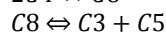
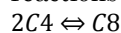
**Figure 3.** Effect of Variation of WHSV on Selectivity of Butenes, Propylene and Pentens using the Pure 1-Butanol Feed (Reaction Temperature is Set to 480 °C)

Butanol dehydration is a facile reaction and takes place over many acidic catalysts at low temperatures (Zhang et al., 2010). The 1-butanol dehydrates on acidic zeolite catalysts to produce olefins (Zhang et al., 2011).

Since the dehydration reaction of 1-butanol to butenes is rapid and instantaneous, the complete conversion of 1-butanol, as shown in Fig 2, is expected. The selectivity of butenes is greater than 80% and propylene and pentenes are the by-products of the reactions. The reaction pathway reveals that the oligomerization of butenes and cracking of the heavy components are the major contributors in propylene production. Propene and pentene constitute the main components of the products, which are the expected products of the C<sub>8</sub> cracking reaction; C<sub>8</sub> species are mainly produced by butenes dimerization (Wu and Kaeding, 1984; Wu et al., 2011).

As shown in Fig 3, a decrease in WHSV, the selectivity of pentene becomes lower than that of propene due to the secondary reactions of pentene. Since, ethylene and hexenes are

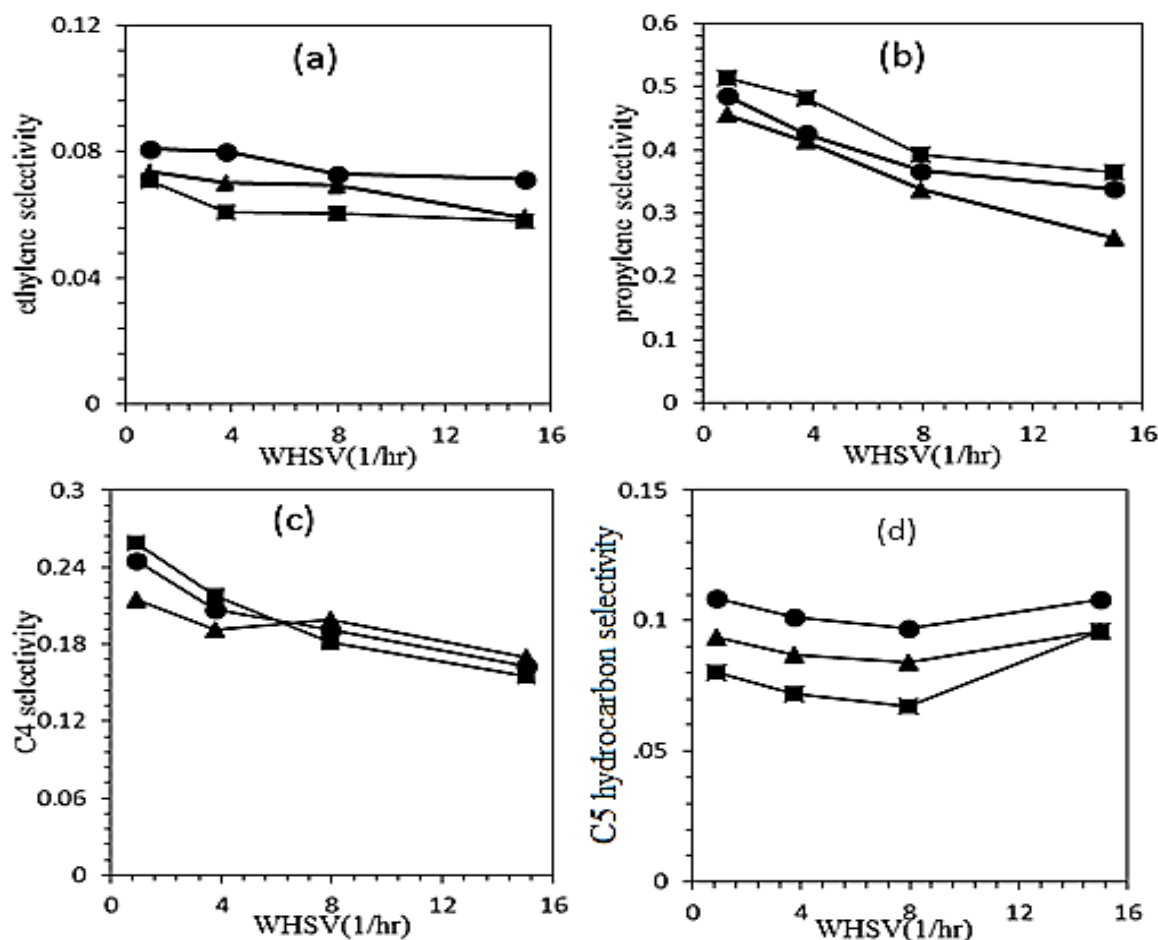
detected in trace amounts; the primary reactions for butenes are expressed as follows:



Therefore, 1-butanol acts as a precursor for production of butenes and propylene is produced from butenes by following the above proposed pathway.

### 3.2. Reaction of Pure Methanol

Conversion of methanol over the H-ZSM-5 zeolite catalyst produces water, a complex mixture of hydrocarbons and a small amount of alcohols (Menges & Kraushaar-Czarnetzki, 2012). In order to assess the methanol conversion on H-ZSM-5 catalyst in experiments, a mixture of (50-50) wt.% of methanol and water is fed to the reactor; the presence of water decelerates the catalyst deactivation and methanol decomposition to carbon and formaldehyde. The selectivity of main olefins at three different temperatures of 440, 460, 480 °C and space velocity range of 0.9 hr<sup>-1</sup> to 15 hr<sup>-1</sup> is illustrated in Fig.4.



**Figure 4.** Effect of Temperature on Selectivity of Ethylene (a), Propylene (b), Butanes (c) and C<sub>5</sub> Hydrocarbons (d) at Different WHSV using the Pure Methanol. 440 °C (▲), 460 °C (●) and 480 °C (■).

As observed here, the propylene selectivity increases with an increase in temperature while the selectivity of C<sub>5</sub> heavy compounds decreases. This fact can be explained due to an increase in the rate of cracking reactions together with an increase in the reaction temperature. The selectivity of ethylene (Fig 4a) and butenes (Fig 4d) have no significant variation upon a change in the reaction temperature, while the propylene selectivity (Fig 4b) further increases at the cost of reducing the C<sub>5</sub> selectivity. The maximum propylene selectivity is recorded as 50% at 480 °C and WHSV of 0.9 1/hr. An increase/decrease in space time/WHSV increases the selectivity of propylene and other light olefins and decreases the selectivity of heavy olefins like C<sub>5</sub>. This trend is caused by the secondary reactions like dimerization and methylation of olefins. Heavy hydrocarbons are mainly formed by methylation of the light olefins at higher space times.

### 3.3. The 1-Butanol and Methanol Co-Feeding

In order to reduce the amount of experiments, the design of experiments with RSM method is applied. This method is applied in order to optimize the propylene selectivity and get the parameter that gives the best response. In statistics, response surface methodology (RSM) explores the correlation between the several explanatory variables and one or more response variables. The main idea of RSM is to

apply a sequence of designed experiments to obtain an optimal response. In this case, the level of parameters must be specified.

Here, the effect of temperature, concentration of 1-butanol and WHSV are examined on the appropriate response (propylene selectivity). Operational constraints do not allow for a wide range of parameters to be selected. For example, the propylene selectivity is not appropriate at temperatures below 440 °C; temperatures above 490 °C are not recommended because of catalyst deactivation; therefore, the temperature range of 440-490 °C is suggested. Space velocity levels are chosen based on the limitations of the methanol that is converted. In the space velocity above 15 hr<sup>-1</sup>, conversion rate of methanol is very low. Since in very low space velocities, the capacity of propylene production is not economical feasible, the space velocity range of 0.9 -15 hr<sup>-1</sup> is selected.

The selected range for variation of the 1-butanol concentration is based on the thermodynamic limitations and catalyst deactivation (Brike et al, 2011). Increasing the concentration of heavy compounds on the surface of the catalyst accelerates the catalyst deactivation. Therefore caution must be, in the MTP process, when the produced heavy hydrocarbons are recycled into the reactors inlet. Based on the selected levels for effective variables, 20 runs are suggested by selected experiment method design, Table 1.

**Table 1.** Suggested Runs by Selected Design of Experiment Method

| run | Temperature( °C) | Mass fraction of 1-butanol | WHSV (1/hr) | Selectivity of propylene | Conversion of methanol |
|-----|------------------|----------------------------|-------------|--------------------------|------------------------|
| 1   | 465.00           | 0.13                       | 7.95        | 0.4566                   | 0.8913                 |
| 2   | 465.00           | 0.13                       | 0.90        | 0.6860                   | 0.9857                 |
| 3   | 465.00           | 0.13                       | 7.95        | 0.4601                   | 0.8890                 |
| 4   | 465.00           | 0.25                       | 7.95        | 0.3588                   | 0.9011                 |
| 5   | 450.13           | 0.05                       | 12.14       | 0.5100                   | 0.8347                 |
| 6   | 465.00           | 0.13                       | 7.95        | 0.4516                   | 0.8903                 |
| 7   | 479.87           | 0.20                       | 12.14       | 0.4140                   | 0.8420                 |
| 8   | 465.00           | 0.13                       | 15.00       | 0.3100                   | 0.7131                 |
| 9   | 465.00           | 0.00                       | 7.95        | 0.4148                   | 0.8991                 |
| 10  | 465.00           | 0.13                       | 7.95        | 0.4560                   | 0.8847                 |
| 11  | 479.87           | 0.05                       | 12.14       | 0.4956                   | 0.945                  |
| 12  | 490.00           | 0.13                       | 7.95        | 0.4744                   | 0.8900                 |
| 13  | 450.13           | 0.20                       | 12.14       | 0.3556                   | 0.8428                 |
| 14  | 450.13           | 0.05                       | 3.76        | 0.5070                   | 0.9581                 |
| 15  | 465.00           | 0.13                       | 7.95        | 0.4600                   | 0.8920                 |
| 16  | 450.13           | 0.20                       | 3.76        | 0.4504                   | 0.9421                 |
| 17  | 440.00           | 0.13                       | 7.95        | 0.4197                   | 0.8509                 |
| 18  | 465.00           | 0.13                       | 7.95        | 0.4497                   | 0.8900                 |
| 19  | 479.87           | 0.20                       | 3.76        | 0.6500                   | 0.9539                 |
| 20  | 479.87           | 0.05                       | 3.76        | 0.5500                   | 0.9626                 |

To have less error rate, each test is repeated three times. The propylene selectivity of optimization, call graph from the RSM method is shown in Fig. 5.

As depicted in Fig 5, the maximum selectivity of propylene is achieved at WHSV of 0.9 hr<sup>-1</sup>, 13 wt% of 1-butanol and at 480 °C temperature reaction. According to Table2, in ANOVA analysis, applied on the parameters of RSM method, the Values of "Prop > F" are less than 0.05, indicating that the model terms are significant. In this study the WHSV, temperature and 1-butanol concentration are

significant model terms and WHSV is very significant compared to other parameter.

Lack of fit for this model is very low ( $LF=4.865E-003$ ), thus, it can be deduced that the model is significant. The ideal Ri-squared is 0.03. A high Ri-squared means the model terms are correlated to one another, leading to poor models. So, there is no significant cross-correlation among the parameters of the considered model. Validity of the optimal point provided by the experiment design is tested. In these conditions, the propylene selectivity is 68%, an acceptable value.

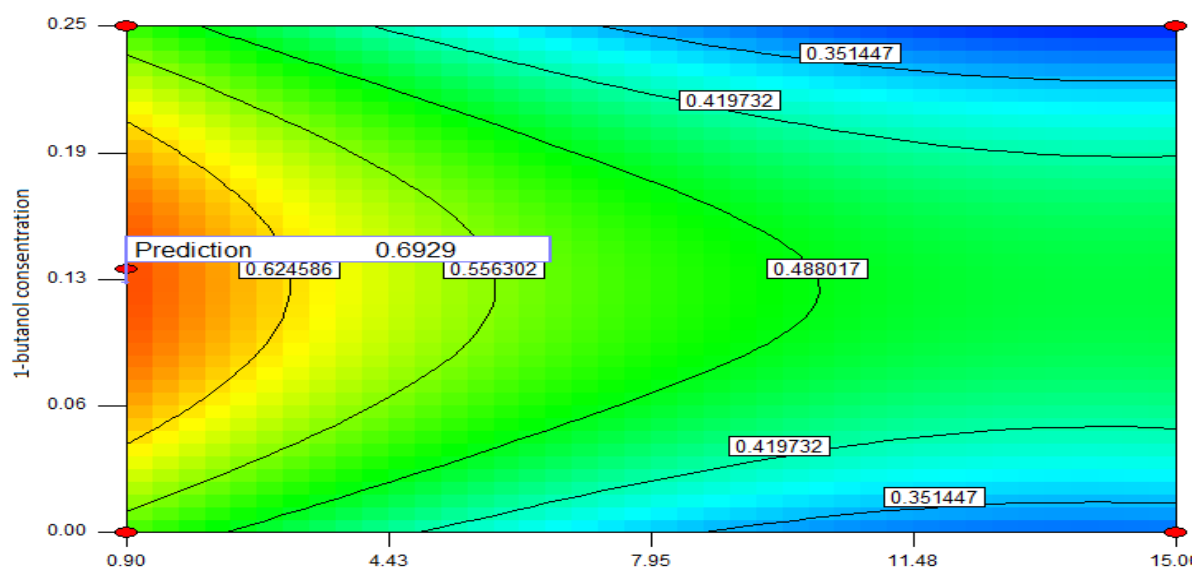


Figure 5. Contour Map for Maximum Selectivity of Propylene in Optimum Reaction Conditions

Table 2. ANOVA Table for Parameters in Design of Experiment

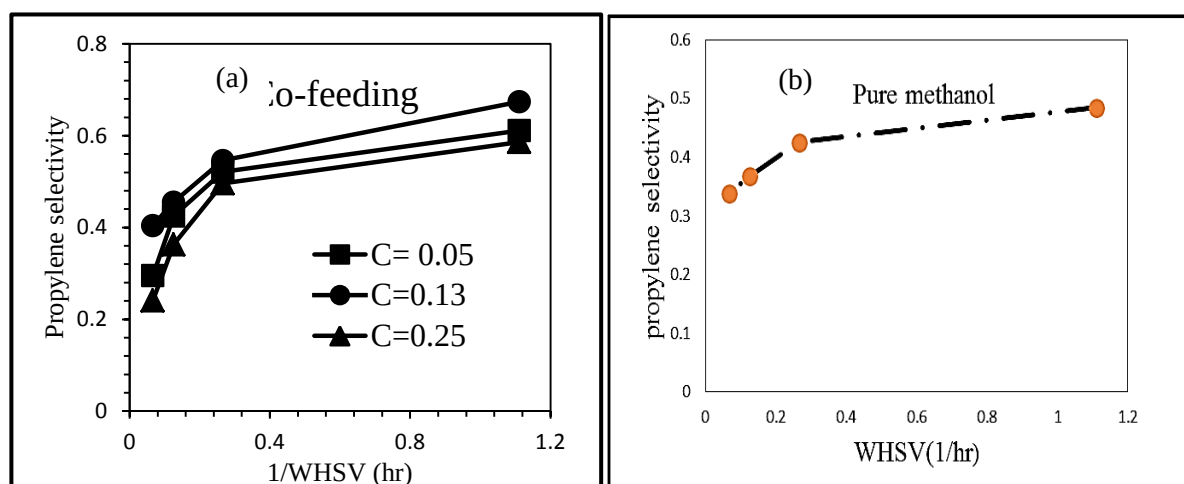
|        | Sum of   | Mean     | F        | p-value  |             |
|--------|----------|----------|----------|----------|-------------|
| Source | Squares  | Square   | Value    | Prob > F |             |
| Model  | 0.079867 | 0.026622 | 9.133068 | 0.0009   | significant |
| A-temp | 0.006475 | 0.006475 | 2.221404 | 0.0315   |             |
| B-cons | 0.009787 | 0.009787 | 3.357644 | 0.0094   |             |
| C-WHSV | 0.063604 | 0.063604 | 21.82016 | 0.0003   |             |
| AB     | 0.00738  |          | 2.27     | 0.1631   |             |
| AC     | 0.00567  |          | 1.74     | 0.2164   |             |
| BC     | 0.00431  |          | 0.44     | 0.5224   |             |
| A^2    | 0.000046 |          | 0.014    | 0.9071   |             |
| B^2    | 0.00553  |          | 1.7      | 0.2217   |             |
| C^2    | 0.0056   |          | 1.74     | 0.2156   |             |

### 3.4. Comparison between the Propylene Selectivity using Co-Feeded and Pure Methanol

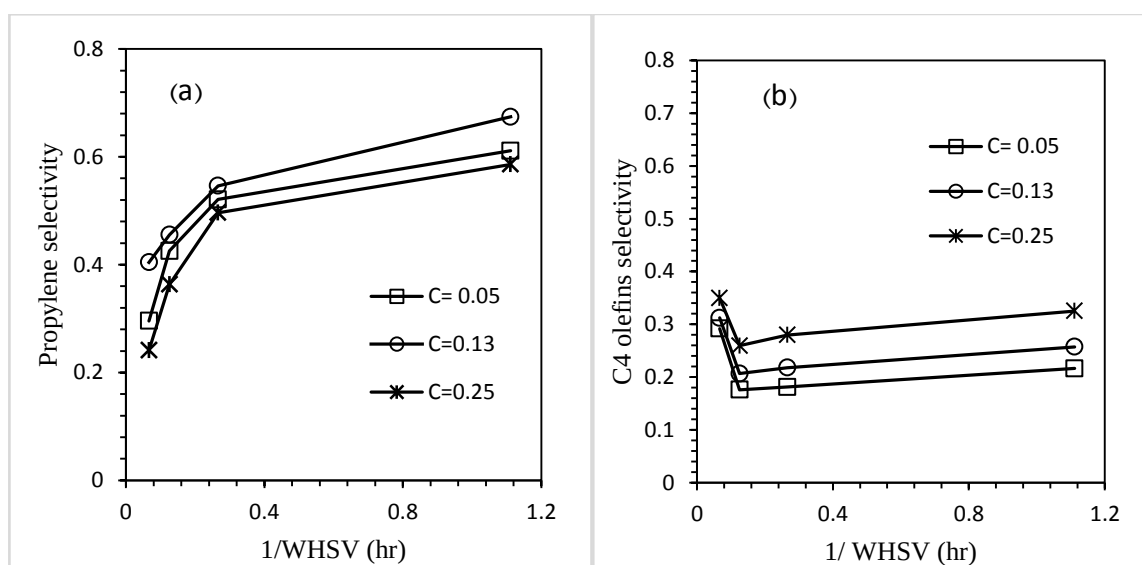
The selectivity of propylene where three different concentration of 1-butanol as co-feed component and pure methanol are applied at 480 °C is compound in Fig. 6.

As observed in Fig 6a, using a mixture of methanol and 13% wt of 1-butanol increases the propylene selectivity by 28% compared to the pure methanol Fig 6b. The 1-butanol concentration below 13 wt%, increases the selectivity of propylene, and the same the

above 13%wt slightly reduces the propylene selectivity. This behavior is due to secondary reactions between olefins, like skeletal isomerization of butenes (John et al., 2015; Wattanakit et al., 2012). With an increase in the concentration of butenes in surface of the catalyst and a decrease in the methanol concentration, methylation of light olefins and cracking of the higher hydrocarbons are suppressed, allowing the skeletal isomerization to become the main reaction pattern. There exists an indirect relation between 1-butanol and propylene selectivity rates, Fig. 7.



**Figure 6.** Propylene Selectivity for (a) Methanol Co-Feeding with 1-Butanol at Three Different Concentration Level (b) Pure Methanol at Temperature of 480 °C



**Figure 7.** Effect of 1-Butanol Concentration on the Selectivity of Propylene (a), Butenes (b), at Different WHSV Reaction Conditions. Reaction Temperature is Set to 480 °C

## 5. Conclusion

Propylene selectivity of 69% is achieved by feeding a mixture of 13 wt% 1-butanol, 37 wt% of methanol and 50 wt% of water at reaction temperature of 480 °C with space velocity of 0.9 hr<sup>-1</sup>. This result indicates that the selectivity of propylene increases by 28% in presence of 13 wt% of 1-butanol compared to the pure methanol. According to experiment design method, WHSV of P-value of 0.0003, feed composition with P-value of 0.0094, and reaction temperature with P-value of 0.03 constitute the most effective parameters on the propylene selectivity, respectively.

## Nomenclature

|                       |                                               |
|-----------------------|-----------------------------------------------|
| $F_{M, \text{input}}$ | Input mole flow rate of methanol              |
| $F_{M, \text{out}}$   | Output mole flow rate of methanol             |
| $F_{b, \text{input}}$ | Input mole flow rate of 1-butanol             |
| $F_{b, \text{out}}$   | Output mole flow rate of 1-butanol            |
| $F_i$                 | Mole flow rate of the $i^{\text{th}}$ species |
| $p$                   | Number of species                             |

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