

# Production of gasoline range hydrocarbons from catalytic reaction of methane in the presence of ethylene over W/HZSM-5

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## Abstract

The catalytic conversion of a methane and ethylene mixture to gasoline range hydrocarbons has been studied over W/HZSM-5 catalyst. The effect of process variables, such as temperature, percentage of volume of ethylene in the methane stream and catalyst loading on the distribution of hydrocarbons was studied. The reaction was conducted in a fixed-bed quartz-micro reactor in the temperature range of 300–500 °C using percentage of volume of ethylene in methane stream between 25 and 75% and catalyst loading of 0.2–0.4 g. The catalyst showed good catalytic performance yielding hydrocarbons consisting of gaseous products along with gasoline range liquid products. The mixed feed stream can be converted to higher hydrocarbons containing a high-liquid gasoline product selectivity (>42%). Non-aromatics C<sub>5</sub>–C<sub>10</sub> hydrocarbons selectivity in the range of 12–53% was observed at the operating conditions studied. Design of experiment was employed to determine the optimum conditions for maximum liquid hydrocarbon products. The distribution of the gasoline range hydrocarbons (C<sub>5</sub>–C<sub>10</sub> non-aromatics and aromatics hydrocarbons) was also determined for the optimum conditions.

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**Keywords:** Gasoline range hydrocarbons; Catalytic conversion; Methane and ethylene mixture; Design of experiment; Optimum condition

## 1. Introduction

An excess consumption of petroleum resources has become significantly critical problems that may lead to acute energy crisis. Utilization of natural gas and coal has been considered as an effective way to reduce the dependence on liquid oil consumption. The transformation of methane (the

main component of natural gas) to useful higher hydrocarbons and fuel can be performed by indirect and direct processes, which are carried out with and without passing through the syngas formation, respectively. Recently, the manufacture of synfuels from natural gas is available for large scale as demonstrated by the MTG plant and the Fischer–Tropsch (FT) by using indirect process technologies. Nevertheless, many attempts are being made to convert natural gas into liquid hydrocarbons by the direct method without passing through the intermediate syngas formation [1]. The direct conversion of methane to C<sub>2</sub> hydrocarbons via oxidative coupling of methane (OCM) has attracted academic and industrial interests due to its potential to be an effective method to utilize natural gas for industrial feedstocks. However, the usefulness of this process has been limited so far as it has low methane conversion and/or low hydrocarbons selectivity [2]. An approach to overcome the limitation of OCM process was reported and it consisted of a two-step process [3]. In the first step, methane or natural gas is converted into lower olefins, which is transformed

*Abbreviations:* ANOVA, analysis of variance; BET, Brunauer–Emmet–Teller; CCD, central composite design; DF, degree of freedom; FID, flame ionization detector; FT, Fischer–Tropsch; GC, gas chromatography; MS, mean square; MTG, methanol to gasoline; OCM, oxidative coupling of methane; RSM, response surface methodology; R<sup>2</sup>, the coefficient of determination; Si/Al, silicon to aluminium ratio; SS, sum of squares; SSE, sum of squares due to residuals; SSR, sum of squares due to regression; SST, total of sum of squares; TCD, thermal conductivity detector; ZSM-5, zeolite secony mobil five

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directly into gasoline range hydrocarbons over a pentasil zeolite catalyst. More recently, Alkhalwaleh et al. [4] reported the conversion of methane into higher molecular weight hydrocarbons. In their study, methane is first converted into acetylene, which is followed by hydrogenation into ethylene. Then, the ethylene in a feed mixture comprising of methane was reacted over a catalyst to produce higher molecular weight hydrocarbons. It is therefore of great practical interest to convert dilute ethylene without being separated from the methane streams into a much less volatile product(s), such as gasoline hydrocarbons. In another development, the conversion of methane to higher hydrocarbons in the presence of ethylene proceeded over silver cations-loaded H-ZSM-5 (Ag/H-ZSM-5) [5]. Due to the increasing interest in the production of sulfur-free transportation fuels via lower olefins oligomerization, the optimization study on oligomerization of feed mixture containing methane and ethylene to produce higher hydrocarbons in the gasoline range over W/HZSM-5 is reported in this paper. The effect of process variables, such as temperature, percentage of volume of ethylene in the methane stream and catalyst loading on the distribution of hydrocarbons was studied according to statistic method with the application of design of experiment utilizing the STATISTICA software (Version 6.0; Statsoft Inc.).

## 2. Experimental procedure

### 2.1. Catalyst preparation

The 2 wt.% W/HZSM-5 catalyst was prepared by impregnation method. NH<sub>4</sub>ZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 30; Zeolyst international Co. Ltd.) was converted to HZSM-5 by calcinations at 500 °C for 4 h. It was then impregnated with calculated amount of the aqueous solution of ammonium tungstate (NH<sub>4</sub>)<sub>5</sub>H<sub>5</sub>[H<sub>2</sub>(WO<sub>4</sub>)<sub>6</sub>]·H<sub>2</sub>O (A. R.). The sample was dried at 110 °C overnight and calcined at 550 °C for 5 h. The catalyst was crushed and sieved into the size of 35–60 mesh for catalytic testing.

### 2.2. Activity testing

Catalytic testing was carried out at atmospheric pressure in a fixed-bed continuous flow system with a quartz reactor of 9 mm internal diameter and 300 mm length. Before reaction, the catalyst was pretreated in a flow of nitrogen at

Table 1  
Properties of HZSM-5 zeolite and W/HZSM-5 catalysts

Properties	HZSM-5	W/HZSM-5
Si/Al ratio	30	30
BET surface area (m <sup>2</sup> /g)	400	372
Pore size (nm)	0.53 × 0.56	Not available
Acidity (mmol NH <sub>3</sub> /g)	1.251	1.164

100 ml min<sup>-1</sup> for 1 h at 550 °C. A gas mixture comprised of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and N<sub>2</sub> (N<sub>2</sub> was used as internal standard) was introduced into the reactor containing the catalyst. Catalytic reactions were performed with different reaction variables based on central composite design (CCD) method. The gaseous products was analyzed by an on-line HP 5890 series II GC-TCD equipped with Porapak Q and molecular sieve 5A columns for separation of N<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>, while UCW 982 12% and DC 200 26% columns were used to separate the lower hydrocarbons including C<sub>3</sub>–C<sub>5</sub> hydrocarbons. The liquid products comprised of C<sub>5</sub><sup>+</sup> non-aromatics and aromatics hydrocarbons were analyzed on FID chromatograph equipped with HP-1 capillary column (Table 1).

## 3. Results and discussion

The study was performed based on design of experiment (DOE) method. The statistical method of factorial DOE eliminates the systematic errors with an estimate of the experimental error and minimizes the number of experiments [6,7]. A central composite design with three process variables was used. According to the CCD, the total number of experiments conducted is 16 with 2<sup>3</sup> two-level factorial design, two central points and six star points [8]. Each variable consists of three different levels from low (–1), to medium (0) and to high (1). The level value of star point is ±1.287 to make a central composite orthogonal design. The independent variables used in the statistical study were temperature, ethylene concentration in the feed mixture containing methane and ethylene, and catalyst loading. Table 2 presents the independent variables with the operating range of each variable. The levels of the independent variables were chosen based on a previous study reported in the literature [5].

The reaction of methane and ethylene mixture over W/HZSM-5 catalyst produced liquid hydrocarbons with high selectivity to gasoline range. The outlet reactor stream

Table 2  
Independent variables with the operating range of each variable

Independent variables	Notations	Levels value				
		–1.287	–1	0	+1	+1.287
Temperature (°C)	X <sub>1</sub>	271	300	400	500	529
Ethylene concentration in a methane-ethylene mixture	X <sub>2</sub>	0.19	0.25	0.50	0.75	0.82
Catalyst loading	X <sub>3</sub>	0.17	0.2	0.3	0.4	0.43

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