

# *A Four-lumped Kinetic Model to Study Propene Oligomerization Over HZSM-5 Zeolite*

L. Shirazi<sup>i</sup>; M. R. Ghasemi<sup>ii</sup>; E. Jamshidi<sup>iii</sup>

## **ABSTRACT**

In this paper study kinetic of propene oligomerization reaction over HZSM-5 zeolite is studied and kinetic parameters such as rate constant and activation energy are evaluated. Initially, a number of reactions are carried out over HZSM-5 zeolite with different Si/Al ratios (10-50) at atmospheric pressure, with temperature in the range of 250 - 400 °C and GHSV = 195-1170 h<sup>-1</sup>; this leads to the conclusion that the highest quantity of C<sub>7</sub><sup>+</sup> hydrocarbons is obtained for HZSM-5 of Si/Al molar ratio = 25. The zeolite with Si/Al ratio of 25 is then chosen for the kinetic study. A four-lumped kinetic model based on reactant and the reaction products is used to describe the propene oligomerization. The kinetic parameters of this model are fully determined by using a non-linear regression on experimental data. Products yield predicted by this model is in agreement with experimental data.

## **KEYWORDS**

HZSM-5, zeolite, propene oligomerization, kinetic study.

## **1. INTRODUCTION**

The oligomerization of light olefins over acid type catalysts is an important process for the production of gasoline and distillate fuels [1,2]. The use of ZSM-5 zeolite for oligomerization of light olefins was proposed in 1970's by Mobil, known as 'Mobil Olefins to Gasoline and Distillate' (MOGD) [3]. Due to shape selectivity and acid properties of ZSM-5 zeolite, this catalyst then replaced the classical phosphoric acid catalyst for oligomerization [4]. Apart from its high selectivity and activity due to its structure and Si/Al ratio, which reflects the number and strength of the acid sites, the low deactivation rate of ZSM-5 zeolite as compared to other types of zeolites, is also another important factor for its catalytic behavior [5,6].

Propene oligomerization over ZSM-5 zeolite with different Si/Al ratios was studied at different temperatures and GHSV [7-13]. The hydrocarbon produced at 277 °C and above was predominantly gasoline rather than distillate and as temperature was reduced, the product was much heavier hydrocarbons (C<sub>11</sub>-C<sub>20</sub>). The effect of Si/Al ratio of ZSM-5 in the range of 20-500 on propene oligomerization was investigated and it showed that hydrocarbon products of up to C<sub>12</sub> increased when the

Si/Al decreased [14]. This is in agreement with the work done by Gnep et al. [15], where it was found that in propene oligomerization over ZSM-5 with Si/Al ratio of 30 at 300 °C, hydrocarbon products of up to C<sub>12</sub> were produced.

Several papers have been published on the kinetics of light olefins oligomerization reaction, covering different reaction conditions [16-22]. Quann *et al.* [18] described the kinetic model, which utilizes a detailed carbon number distribution approach, incorporates complex oligomerization and cracking reaction networks. A single kinetic model by Borges *et al.* [22] was developed on the basis of Langmuir-Hinshelwood-Hougen-Watson theory. The reaction rate of oligomerization was described by the same model by Peratello *et al.* [20]. Using the estimated activation energies they concluded that the oligomerization was limited by mass transfer.

In this work catalytic activity of HZSM-5 zeolite with Si/Al molar ratios in the range of 10-50 for propene oligomerization at atmospheric pressure, temperature in the range of 250 - 400 °C and GHSV = 195-1170 h<sup>-1</sup> was investigated. A four-lumped kinetic model based on reactant and the reaction products using optimum conditions (i.e., Si/Al = 25 and temperature 250-300 °C) was then proposed.

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## 2. EXPERIMENTAL

### A. HZSM-5 Preparation and Characterization

The Na-ZSM-5 zeolite with Si/Al molar ratios in the range of 10-50 was synthesized and then transformed into HZSM-5 using the ion-exchange method. Techniques such as XRD, FT-IR, SEM, EDX, TG-DTA, BET and NH<sub>3</sub>-TPD were used to characterize the zeolite. Details of the preparation and characterization of the zeolite are previously have been described in [23]. In this study, HZSM-5 zeolites with Si/Al molar ratio values of 10, 25, 40 and 50 were used.

### B. Propene Oligomerization

#### 1) Laboratory Set-up

The laboratory set-up used to study the catalysts activity and kinetic measurements for propene oligomerization is shown in Figure 1. The set up consists of a tubular stainless steel reactor with 0.9 cm i.d. and 40 cm long housed in a three-zone heating jacket, a temperature controller to maintain the heating rate and the temperature of the jacket as well, a mass flow controller (Brooks Model 5850), a separator and a GC to analyze the product.

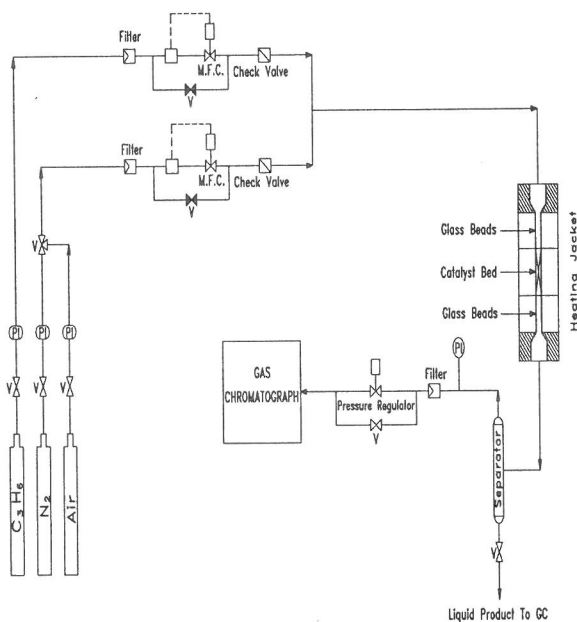


Figure 1: Set-up used for propene oligomerization

#### II) Procedure

The prepared zeolite powder was converted into disk-shaped pellets of 2 mm thickness and 10 mm diameter. The pellet were then broken and sieved into particles which were approximately 0.5 mm in. The reactor was loaded with fresh catalyst for each experiment (Figure 1).

Prior to each experiment the reactor was heated up to 550 °C under a flow of N<sub>2</sub> at atmospheric pressure and kept at this temperature for 2 h. The reactor was then

allowed to cool down to the reaction temperature, under the flow of N<sub>2</sub>. After reaching the desired temperature (250-400 °C), the reactor was maintained for 1 h at that temperature. The nitrogen flow was then stopped and propene was fed to the reactor through the Mass Flow-Controller (MFC). A thermocouple was placed at the center of the catalyst bed to observe the temperature change during the reaction. The gas products were analyzed using a PU 4600 Philips gas chromatograph, which connected on-line to the set-up. The liquid products were collected in the separator and analyzed using a CP 3800 gas chromatograph equipped with a flame ionization detector, on a petrocol TM DH capillary column. Reaction conditions used in this work for propene oligomerization are given in Table 1.

TABLE I  
REACTION CONDITIONS FOR PROPENE OLIGOMERIZATION\*

GHSV (h <sup>-1</sup> )	Reaction temperature (°C)
195-1170	250 - 400

\* All reactions were carried out at atmospheric pressure.

## 3. RESULTS AND DISCUSSION

### A. Oligomerization of propene over HZSM-5 zeolite

The liquid hydrocarbon product distribution during the propene oligomerization reaction, over HZSM-5, with different Si/Al molar ratios, at different temperatures and GHSV are shown in Figure 2.

The results showed that the product selectivity changed with the aluminum content of the zeolite and since the aluminum content attributes to the activity of the zeolite, therefore for a desirable activity for oligomerization reaction, the aluminum content of the zeolite plays an important role. As it is shown in [23], the change in Si/Al molar ratios not only changed the activity of the zeolite, but also affected the crystal size. It can be concluded that the activity and crystal size of the zeolite, simultaneously affected the hydrocarbon product distribution.

Results for hydrocarbon product distribution at different Si/Al molar ratios showed that for all Si/Al molar ratios other than 10, the C<sub>7</sub><sup>+</sup> selectivity decreased with each increase in the Si/Al ratio, this can be postulated as follows; at the Si/Al ratio of 10 a complex effect of acid sites and morphology of the zeolite on all reactions, on the zeolite, make this zeolite behave differently, which can not be correlated only by its Si/Al molar ratio and activity. These effects may be due to the fact that the oligomerization reaction is a structural sensitive reaction, where all the catalyst parameters, such as, crystal size, morphology and Si/Al ratios can affect the product distribution [24].

Taking into account that the production of heavier olefins or oligomers, (i.e., C<sub>7</sub><sup>+</sup>) is the target to reach in oligomerization reaction, it can be seen from the results that at Si/Al =25 the C<sub>7</sub><sup>+</sup> hydrocarbons are at their most. Therefore, it can be concluded that, for propene

oligomerization, the optimum ratio of Si/Al is 25. This shows that Si/Al ratio of zeolite has a pronounced effect on product distribution for oligomerization reactions.

The increase in GHSV can always change the product distribution during a catalytic reaction. This effect was also noted in this work. As it can be seen from Figure 2, the highest amount of  $C_7^+$  hydrocarbon produced at different temperatures was obtained at GHSV = 195  $h^{-1}$ , whereas at higher GHSV, the amount of  $C_7^+$  hydrocarbon, decreased.

Figure 2 shows that temperature rise had two distinct effects, increase in temperature from 250 °C to 300 °C, increased the oligomerization (i.e., production of  $C_7^+$  hydrocarbons), while at temperature above 300 °C, the production of lighter olefins (i.e.,  $< C_7$  hydrocarbons)

increased. This is an indication that the cracking of heavier olefin to lighter olefin increases with rise in temperature. This effect can be seen clearly in Figure 3.

As shown, parameters such as temperature and GHSV simultaneously affected the production of different hydrocarbon products.

It is postulated by Quann *et al.* [18] that, in oligomerization reaction, propene will oligomerize to  $C_6$ ,  $C_9$ ,  $C_{12}$ , etc. oligomers. These then isomerize and reack, forming a range of light olefins. Lastly, these reoligomerize to an equilibrium distribution of heavier iso-olefin. As a result of having both forward (oligomerization) and reverse (cracking) reactions, a continuous carbon number distribution, occurs in the product.

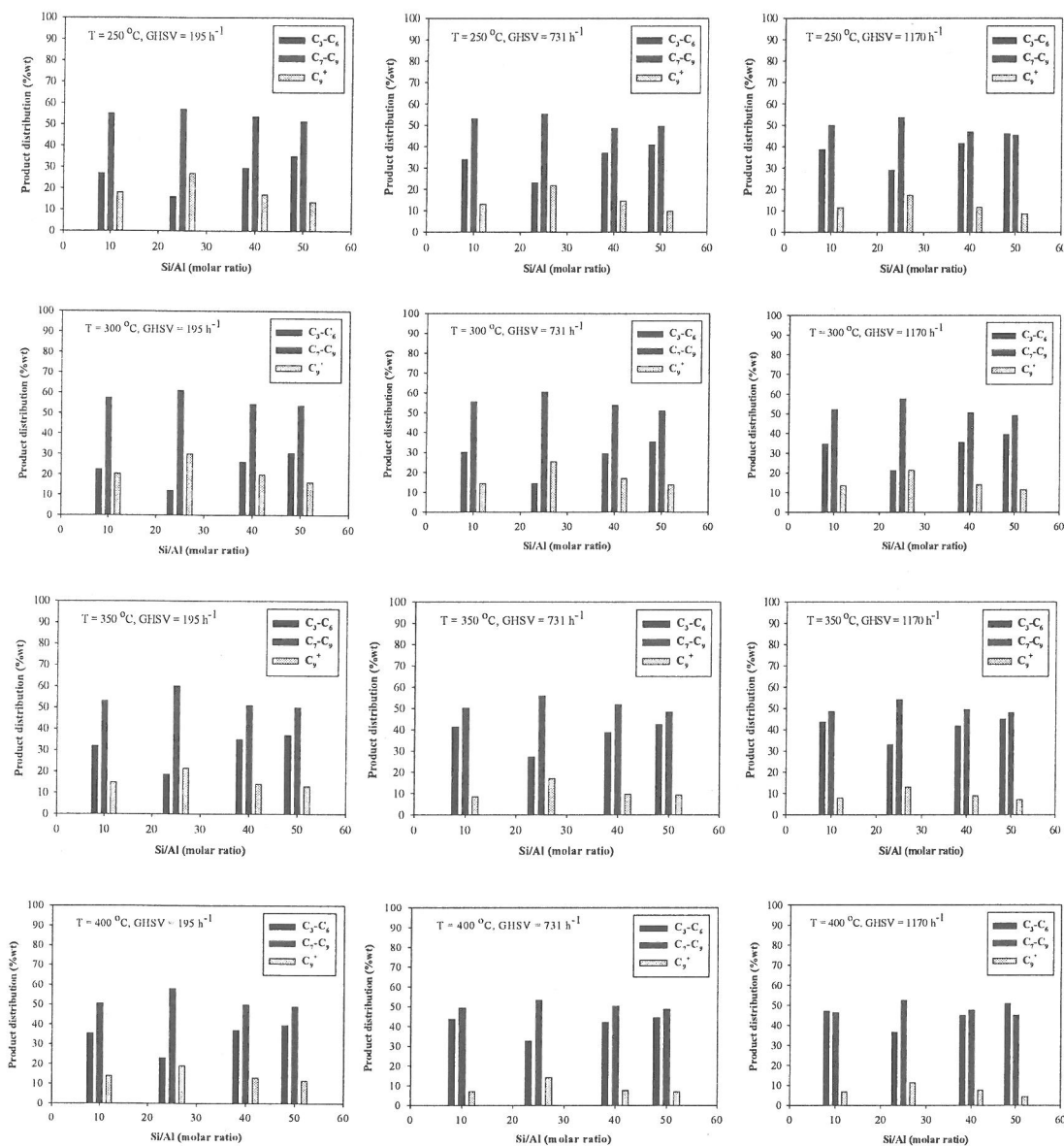


Figure 2: Liquid product distribution obtained for propene oligomerization at atmospheric pressure, various temperatures and GHSV on HZSM-5 with different Si/Al molar ratios.

The effect of temperature on hydrocarbons produced, during propene oligomerization reaction over HZSM-5 with Si/Al molar ratio of 25 and GHSV = 195 h<sup>-1</sup> is shown in Figure 4. As it can be seen, at 250 °C, the amount of olefin & aromatic produced is 56.85 wt% and 7.58 wt%, respectively, whereas at 400 °C, these amounts had been changed to 28.99 wt% and 16.74 wt%. It can then be concluded that, at a lower temperature, oligomerization of olefins is the dominant reaction. A significant quantity of paraffins, presumably as a result of hydrogen transfer processes is also produced. A rise in temperature, increased the formation of aromatics, naphthenes (cycloalkanes) and paraffins [25].

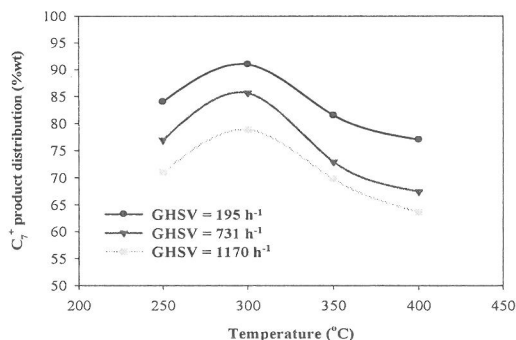


Figure 3: Effect of temperature on C<sub>7</sub><sup>+</sup> product distribution for propene oligomerization at various GHSV on HZSM-5 with Si/Al molar ratio of 25.

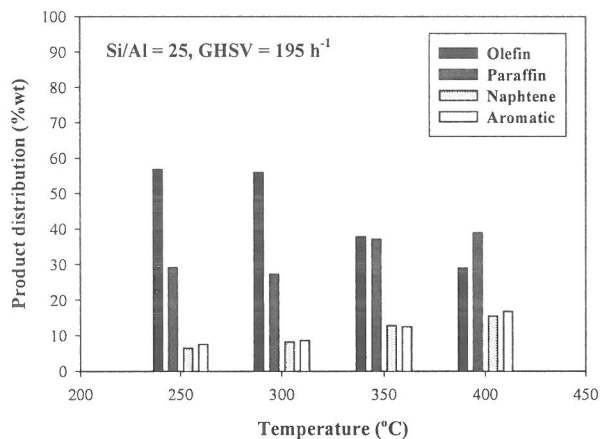


Figure 4: Liquid product distribution obtained for propene oligomerization at atmospheric pressure, GHSV = 195 h<sup>-1</sup> and different temperatures on HZSM-5 with Si/Al molar ratio of 25.

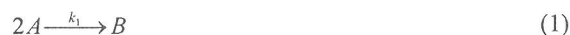
It can be seen from the results that the amount of C<sub>7</sub><sup>+</sup> hydrocarbons produced over zeolite with Si/Al = 25 at 300 °C and GHSV = 195 h<sup>-1</sup> is the highest (91 wt %) and is the lowest (63.6 wt %) at 400 °C with GHSV = 1170 h<sup>-1</sup> (Figure 3).

#### B. Kinetic study

During the catalyst performance evaluation it was observed that above 300 °C the cracking reaction together with oligomerization reaction take place, in order to avoid

the cracking reaction, the kinetic has been studied over zeolite with Si/Al = 25 within the temperature range of 250-300 °C and a range of catalyst to feed ratios (W/F = 4-20 g cat./mole C<sub>3</sub>H<sub>6</sub>/h).

The kinetic study in this work is based on the lumped kinetic model and for that, the most important species in propene oligomerization has taken into account, i.e., Propene (A) = (C<sub>3</sub>H<sub>6</sub>), Dimer (B) = (C<sub>3</sub>-C<sub>6</sub>), Trimer (C) = (C<sub>7</sub>-C<sub>9</sub>) and Tetramer<sup>+</sup> (D) = (C<sub>9</sub><sup>+</sup>). Therefore a four-lumped model was used and the following reactions, assumed:



The following kinetic expressions were formulated as a function of product concentration and kinetic constants. This model has seven kinetic constants.

$$r_A = -2k_1C_A^2 - k_2C_A C_B - k_3C_A C_C - 3k_4C_A^3 + k_6C_C \quad (8)$$

$$r_B = k_1C_A^2 - k_2C_A C_B - k_5C_B C_C + k_6C_C + k_7C_D \quad (9)$$

$$r_C = k_2C_A C_B - k_3C_A C_C + k_4C_A^3 - k_5C_B C_C - k_6C_C + k_7C_D \quad (10)$$

$$r_D = k_3C_A C_C - k_6C_D + k_7C_B C_C \quad (11)$$

For a packed bed catalytic reactor with plug flow of fluid, the following relation is applied [26]:

$$-r_A = \frac{d(X_A)}{d(W/F_A^0)} \quad (12)$$

$$r_{B,C,D} = \frac{d\left(\frac{y_{B,C,D,out} \cdot P}{RT}\right)}{d\left(\frac{W}{\phi_v}\right)} \quad (13)$$

Where  $-r_A$  is the propene reaction rate (mole<sub>A</sub>/h. g cat.),

$X_A$  is conversion of propene,  $F_A^0$  is the feed rate (mole<sub>A</sub>/h),  $W$  is the mass of catalyst (g),  $P$  is the total pressure (kP),  $R$  is the constant of gases (J/mol.K),  $T$  is the temperature (K),  $y$  is the mole fraction and  $\phi_v$  is the volumetric flow rate (cm<sup>3</sup><sub>A</sub>/min).

Based on equation 12, results for propene conversion ( $X_A$ ) against  $\frac{W}{F_A^0}$  was shown in Figure 5. The results are then calculated using this profile and equation 13 are listed in Table 2.

TABLE 2  
Propene conversion and reaction rate at different temperature

Temp. (°C)	$\frac{W}{F_A^0}$ (gcat./mole <sub>A</sub> /h)	$\frac{W}{\phi_v}$ (gcat./m <sup>3</sup> /h)	$X_A$	$C_A$ (mole/m <sup>3</sup> )	$C_B$ (mole/m <sup>3</sup> )	$C_C$ (mole/m <sup>3</sup> )	$C_D$ (mole/m <sup>3</sup> )	$-r_A$ (mole <sub>A</sub> /h.gcat.)	$r_B$ (mole <sub>B</sub> /h.gcat.)	$r_C$ (mole <sub>C</sub> /h.gcat.)	$r_D$ (mole <sub>D</sub> /h.gcat.)
250	4.0	176.34	4.3	22.30	0.518	0.399	0.079	8.22E-03	1.70E-03	1.72E-03	4.55E-04
	12.5	558.04	11	20.73	0.793	1.317	0.453	7.66E-03	-1.77E-04	2.92E-03	1.41E-03
	13.8	614.58	12.1	20.48	0.776	1.497	0.541	7.58E-03	-4.10E-04	3.01E-03	1.49E-03
	16.2	724.70	13.9	20.06	0.708	1.8249	0.708	7.42E-03	-8.30E-04	3.09E-03	1.62E-03
	18.0	804.32	15.2	19.76	0.630	2.0699	0.839	7.30E-03	-1.11E-03	3.10E-03	1.68E-03
	19.3	860.86	16.1	19.55	0.562	2.249	0.937	7.22E-03	-1.29E-03	3.07E-03	1.70E-03
270	4.0	176.34	5.2	21.28	0.532	0.486	0.139	1.07E-02	1.92E-03	2.15E-03	6.65E-04
	12.5	558.04	13.8	19.34	0.823	1.654	0.619	9.80E-03	-2.73E-04	3.72E-03	1.65E-03
	13.8	614.58	15.2	19.02	0.798	1.889	0.728	9.67E-03	-5.33E-04	3.81E-03	1.72E-03
	16.2	724.70	17.5	18.50	0.715	2.296	0.923	9.41E-03	-9.94E-04	3.86E-03	1.80E-03
	18.0	804.32	19.2	18.14	0.625	2.601	1.073	9.23E-03	-1.29E-03	3.81E-03	1.81E-03
	19.3	860.86	20.3	17.89	0.546	2.822	1.183	9.09E-03	-1.48E-03	3.73E-03	1.80E-03
280	4.0	176.34	5.5	20.81	0.537	0.525	0.159	1.15E-02	1.91E-03	2.42E-03	8.16E-04
	12.5	558.04	14.9	18.76	0.802	1.783	0.688	1.05E-02	-3.92E-04	3.95E-03	1.84E-03
	13.8	614.58	16.4	18.43	0.769	2.029	0.804	1.03E-02	-6.64E-04	4.03E-03	1.92E-03
	16.2	724.70	18.8	17.88	0.671	2.463	1.015	1.00E-02	-1.14E-03	4.11E-03	2.02E-03
	18.0	804.32	20.6	17.50	0.568	2.788	1.176	9.81E-03	-1.45E-03	4.08E-03	2.06E-03
	19.3	860.86	21.8	17.23	0.479	3.024	1.296	9.66E-03	-1.65E-03	4.01E-03	2.06E-03
290	4.0	176.34	6.2	20.29	0.568	0.593	0.189	1.31E-02	1.96E-03	3.08E-03	1.12E-03
	12.5	558.04	16.8	18.00	0.811	2.024	0.805	1.18E-02	-4.94E-04	4.29E-03	2.03E-03
	13.8	614.58	18.4	17.66	0.770	2.279	0.927	1.16E-02	-7.84E-04	4.39E-03	2.12E-03
	16.2	724.70	21.2	17.06	0.649	2.765	1.166	1.12E-02	-1.30E-03	4.54E-03	2.26E-03
	18.0	804.32	23.1	16.64	0.527	3.127	1.349	1.09E-02	-1.62E-03	4.59E-03	2.34E-03
	19.3	860.86	24.5	16.34	0.424	3.391	1.484	1.07E-02	-1.83E-03	4.61E-03	2.38E-03
300	4.0	176.34	6.7	19.84	0.568	0.639	0.213	1.42E-02	1.90E-03	3.53E-03	1.35E-03
	12.5	558.04	18.1	17.41	0.776	2.186	0.894	1.26E-02	-6.75E-04	4.51E-03	2.17E-03
	13.8	614.58	19.7	17.07	0.729	2.446	1.020	1.24E-02	-9.88E-04	4.62E-03	2.26E-03
	16.2	724.70	22.7	16.43	0.589	2.964	1.278	1.19E-02	-1.55E-03	4.81E-03	2.43E-03
	18.0	804.32	24.8	15.99	0.451	3.351	1.475	1.16E-02	-1.91E-03	4.92E-03	2.53E-03
	19.3	860.86	26.3	15.68	0.335	3.633	1.621	1.14E-02	-2.15E-03	4.99E-03	2.60E-03

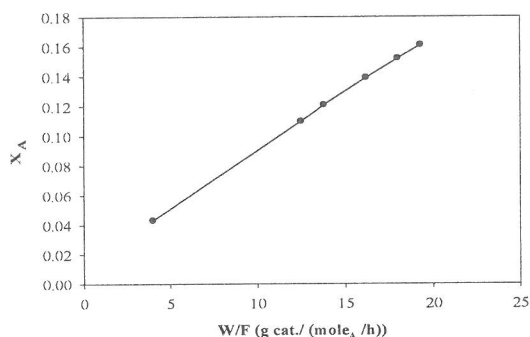


Figure 5:  $X_A$  vs.  $\frac{W}{F_A^0}$  at 250 °C.

Estimation of values for the kinetic parameters involved minimization of error. Using the non-linear least-square regression analysis and applying the results presented in Table 2 to the relations 8 to 11, the kinetic parameters have been calculated. The parameters obtained are listed in Table 3.

The frequency factors and apparent activation energies were estimated according to the Arrhenius relation.

TABLE 3 : KINETIC PARAMETERS

$k$	Temperature (°C)					$k_0$	$-E_{a,app}$ (kJ/mole)
	250	270	280	290	300		
$k_1$	724.23	616.80	553.03	483.55	404.34	1.13	28.31
$k_2$	750.55	665.17	611.04	552.39	476.92	5.05	21.89
$k_3$	785.91	664.22	589.54	503.59	414.51	0.64	31.17
$k_4$	15.44	13.75	12.55	11.12	9.51	0.072	23.55
$k_5$	3.5E-04	3E-04	2.3E-04	1.3E-04	1.24E-04	7.71E-10	57.25
$k_6$	4.95	4.09	3.61	3.09	2.47	2.3E-3	33.62
$k_7$	8.18	6.87	6.08	5.17	4.24	5.4E-3	32.02

#### 4. CONCLUSIONS

The catalytic performance of the HZSM-5 zeolites, with different Si/Al molar ratios, in the range of 10-50, for propene oligomerization at different temperatures and GHSV, was studied in a fixed-bed reactor. The results showed that the hydrocarbon product distribution during oligomerization reaction depends on temperature, GHSV, crystal size, morphology and Si/Al ratio of the zeolite, where the crystal size, morphology and the Si/Al ratio have a conjugative effect on propene oligomerization.

The results showed that the optimum condition for propene oligomerization reaction to produce  $C_7^+$  hydrocarbons, was using a HZSM-5 zeolite with Si/Al molar ratio of 25, at 250 - 300 °C with GHSV = 195  $h^{-1}$ . The kinetic of propene oligomerization reaction was therefore studied at these conditions. A four-lumped kinetic model based on reactant and the reaction products for propene oligomerization was used to describe the propene oligomerization. Good agreement between the model predictions of product yields and experimental data was obtained.

#### 5. ACKNOWLEDGEMENTS

The authors would like to place on record, their appreciation for the support rendered by Research and Technology Directorate / National Iranian Oil Company, on the research leading to the present article.

#### 6. NOMENCLATURE

$-r_A$	propene reaction rate (mole <sub>A</sub> /h. g cat.)
$k$	kinetic rate constant
$X_A$	conversion of propene
$F_A^0$	molar flow rate (mole <sub>A</sub> /h)
$P$	total pressure (kP)
$y$	mole fraction
$C$	concentration (mole/ m <sup>3</sup> )
$\phi_v$	volumetric flow rate (m <sup>3</sup> <sub>A</sub> /min)
$W$	mass of catalyst (g)
$E_{a,app}$	apparent activation energy (kJ/mol)
$R$	universal gas constant (J/mol.K)
$T$	Temperature (K)

#### Superscripts

- Refers to initial concentration

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