

Kinetic modeling of catalytic transformation of methanol and ethanol into hydrocarbons: a review

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Abstract: Several studies have been conducted on the methanol and ethanol conversion to hydrocarbons or olefins. Kinetic modeling helps researchers in interpreting the mechanism of a catalytic reaction and simulating experimental effects. Theoretical methods are valuable tools in this context for investigating experimental results related to mechanism or reactivity. The deterministic kinetic modeling incorporates theory and experimental results, allowing it to illustrate a catalyst in industrial conditions. This review included different kinetic models including the Lumped-Parameter model and Langmuir-Hinshelwood model

Key Word: Kinetic Modeling, Methanol, Ethanol, Lumped-Parameter Model, Langmuir-Hinshelwood model

I. Introduction

Currently, two key technologies for producing lower olefins, primarily ethylene (C₂) and propylene (C₃), are steam and fluid catalytic cracking. Oil and natural gas are used as feedstocks in these technologies. Petroleum and naphtha stocks are reducing, and cracking processes consume a lot of resources. Due to the scarcity of these non-renewable resources, scientists have been encouraged to advance present technology to manufacture chemicals using renewable resources in a better environmentally friendly way. One of the interesting alternatives is the production of olefin compounds and heavier hydrocarbons like gasoline from alcohols such as methanol and ethanol [1].

Prior research has enhanced methanol or ethanol conversions to hydrocarbons or olefins by modifying the catalyst to increase product selectivity, specifying the accurate reaction mechanism, and enhancing the catalyst lifetime. To boost product selectivity, ZSM-5, Al₂O₃, SAPO-34, and amphoteric metal oxide catalysts were modified. However, the catalyst's efficiency needs to be improved even more to minimize coke as well as secondary reactions to aromatic and paraffin [1]. The processes still face several challenges, including control of selectivity, catalyst deactivation, reactions mechanism, process as well as power consumption optimization [1,2].

Kinetic modeling aids researchers in interpreting the mechanism of a catalytic reaction and simulating experimental effects [3]. Catalyst synthesis, structural properties, mechanistic analysis, kinetic evaluation, kinetic modeling, and catalyst deactivation are some of the topics covered by a large number of publications. Theoretical methods are valuable tools in this context for investigating experimental results related to mechanism or reactivity. The deterministic kinetic modeling incorporates theory and experimental results, allowing it to illustrate a catalyst in industrial conditions [4].

The Lumped-Parameter (L-P) model is simpler and involves a much lower compound number in the kinetic scheme. Aside from that, it requires much fewer experimental results [3]. Kinetic modeling applied in the cracking of heavy petroleum fractions is taken as lump format [5]. The L-P model reduces complexity as compared with the case of distributed parameter model (where every component is taken as a single form and not in a lump) by categorizing components into different lumps having similar properties and modifying the reaction pathway among them. As a result, the L-P model is advantageous to have lesser computations involved because of fewer data required which is helpful in reactor designing [2].

Langmuir-Hinshelwood (L-H) model is the widely used kinetic expression to elucidate the kinetics of the catalytic heterogeneous processes. Approximating L-H kinetics to zero-order kinetics is both impossible and inappropriate [6].

Several studies have been conducted on the methanol and ethanol conversion to hydrocarbons or olefins. Taken into account the product formation and the process variables, Ying et al. [7] proposed an L-P model for the transformation of dimethylether (DME) and methanol into olefins using SAPO-34. Aguayo et al. [8] studied the L-P model for the transformation of methanol into lower olefins and gasoline at $T = 673\text{-}823\text{ K}$. Chang et al. [9] revealed a 90% accurate L-H model for the dehydration of ethanol into olefins using H-ZSM-5 catalyst (Si/Al = 70) at $P = 1\text{ atm}$ and $T = 423\text{-}633\text{ K}$. The catalytic reactor was designed using the L-H mechanism. Becerra et al. [10] studied the L-H model for the production of ethylene from aqueous bioethanol using an HZSM-5 catalyst.

This review focuses on different kinetic models of methanol and ethanol such as the L-P model and L-H kinetics model for the production of hydrocarbons (lighter and heavier). Table 1 shows the overall literature reported based on the kinetic models applied.

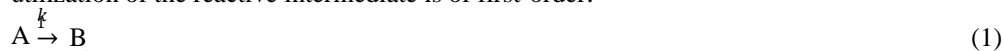
Table no 1 Reported kinetic models used in literature

S.No	Process	Catalysts	Model used	Reference
1.	Methanol to Hydrocarbon	HZSM-5	L-P Model	[11]
2.	Methanol to Hydrocarbon	HZSM-5	L-P Model	[12]
3.	Methanol to Hydrocarbon	HZSM-5	L-P Model	[13]
4.	Methanol to Hydrocarbon	HZSM-5	L-P Model	[14]
5.	Methanol to Hydrocarbon	HZSM-5	L-P Model	[8]
6.	Methanol to Aromatics	Zn modified ZSM-5	L-P Model	[15]
7.	Methanol to Olefins	SAPO-34	L-P Model	[2]
8.	Ethanol to Hydrocarbon	Ca-ZSM-5	L-P Model	[1]
9.	Ethanol to Hydrocarbon	HZMS-5	L-H Model	[10]
10.	Ethanol to Hydrocarbon	HZSM-5	L-P Model	[16]
11.	Ethanol to Hydrocarbon	HZSM – 5	L-P Model	[17]
12.	Ethanol to Hydrocarbon	HZSM – 5	L-P Model	[18]

II. Kinetic modeling of methanol to hydrocarbons

(a) Lumped kinetic model

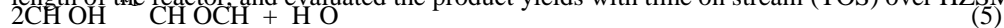
Chang [11] developed a phenomenological kinetic model and described the reaction pathway for the methanol transformation process over ZSM-5. Some assumptions were also made in this model such as (1) methanol as well as DME were always at equilibrium, hence both are taken as single components, (2) generation as well as utilization of the reactive intermediate is of first-order.

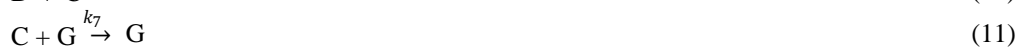


where A, B, C, D represents the oxygenates (methanol + DME), methylene, olefins, paraffins + aromatics, respectively; k_i represents the kinetic constant for i^{th} species, h^{-1} .

The model predicted $k_2 < k_3$, which was evident from the fact that carbene incorporation into C-H bonds was slower than in the case of double bonds. It was observed that this model was able to predict the methanol transformation and its product selectivity with respect to a wide pressure range.

Aguayo et al. [12] suggested a modified Lumped-Parameter model for simulating the reactor to study the process condition effects such as space-time, methanol dilution with nitrogen and water, temperature across the length of the reactor, and evaluated the product yields with time on stream (TOS) over HZSM-5 catalysts.





where A, C, D, G, M, W = oxygenates, water, lower olefins ($C^=$ and $C^=$), and rest hydrocarbons; represents the kinetic constant for i^{th} species, h^{-1} .

With a frequency factor = $6.63 \times 10^6 \text{ atm}^{-1} \text{ min}^{-1}$ and activation energy (E_a) = $27.5 \text{ kcal mol}^{-1}$, the results followed the kinetics of first-order of the amount of coke and the concentration of oxygen. It's worth noting that, while methanol dilution with water in the feed was effective at reducing deactivation, methanol dilution with nitrogen was more effective at reducing temperature peaks in the reactor. It was concluded that a model was proposed which significantly takes into account the water content in the feed and the catalyst deactivation by coking. It was considered that methanol when diluted with water help in reducing the overall deactivation of the catalyst, and when it is diluted with N_2 gas, it helps in reducing the sudden temperature increase due to exothermicity.

Gayubo et al. [13] proposed the Lumped-Parameter model for the transformation of methanol to hydrocarbons over ZSM-5 catalysts, following the same scheme as Aguayo et al. [12]. The proposed kinetic model was validated using data from a fixed bed reactor operating at $T = 573\text{-}723 \text{ K}$ over a wide range of space-time values. At high temperatures, the adsorption of water on the acidic sites of the catalyst was not caused by the reduction of water, but rather because of an obscure impact of water present in the reaction on the mechanisms of product generation. The following findings were also analyzed: DME had high reactivity, either for the formation of olefins (k_3) or for the production of gasoline by alkylation (k_6). The ratio of constants for the oligomerization of olefins (k_4) and cracked gasoline lump (k_8) i.e., (k_4/k_8 ratio) is larger than 50 at $T = 623 \text{ K}$. This ratio decreased with increasing temperature, and at $T = 723 \text{ K}$, the ratio of k_4/k_8 was ~ 5 , implied a significant increase in olefin selectivity. It can be finally concluded that the developed model helps design the reactor with respect to the water content optimization in the feed. The water content in the feed was not considered with respect to the catalyst deactivation, as it was only related to the kinetics in the methanol-to-gasoline (MTG) process. It was observed that at high-temperature cracking is a usual phenomenon. The steps required for methanol to get dehydrated into DME are lessened with the presence of water. The water gets adsorbed on the acid sites of the catalyst is not due to the effect of high temperature, but it is due to some unknown effect of water that is present in the reaction mixture.

Zaidi and Pant [14] proposed a modified kinetic model of Chang [11]. It was observed that up to $T = 673 \text{ K}$ oligomerization, dehydrogenation, cyclization, and aromatization reactions were favored, and olefins were transformed to aromatics. Secondary reactions transform primary olefin products to hydrocarbons in the gasoline range. However, at temperatures above $T = 673 \text{ K}$, cracking and generation of coke occurred over the catalyst. As a result, $T = 673 \text{ K}$ was chosen as the optimal temperature for the MTG reaction. The aromatics yield reduced as the partial pressure of methanol increased ($>90 \text{ kPa}$), while the alkane and olefins yield increased slightly. The validation of the proposed kinetic models was investigated by reducing the error among experimental and theoretical hydrocarbon yields. The proposed kinetic model was:



where A, B, C represent the oxygenates, olefins, aromatics + paraffins, respectively; k_i represents the kinetic constant for i^{th} species, h^{-1} .

The model's performance was good for simulating the laboratory unit. This model considered the disappearance rate of oxygenates by Eq. 1. The $E_a = 80606 \text{ J/mol}$ (Eq. 14) showed olefins as the main products. On another side, taking into account the amount of water in the reaction was essential as it slows down the MTG kinetic scheme steps. The proposed model showed the best fit with the experimental results.

Aguayo et al. [8] studied the Lumped-Parameter of the kinetic model, with elementary reaction steps except for the transformation of olefins into n-butane and lower paraffins ($n = 2$, where n represents the order of reaction). This model well suits the experimental data in the range $T = 673\text{-}823 \text{ K}$. The high reactivity of DME over methanol

was used to obtain a greater depiction of the MTG process kinetics. This increased reactivity was confirmed in the formation of olefins as well as the alkylation of the latter to generate gasoline. As the temperature rises, cracking became more significant, and at $T = 723$ K, the ratio of oligomerization/cracking kinetic constant was 5. Water participates with the methanol adsorption on the acidic sites to a lower extent, and with the adsorption of intermediate oxonium ions in the reaction stages which reduced the dehydration step DME from methanol more evidently. The MTG kinetics, where the olefins and gasoline are in the form of lumps are produced in the range of $T = 573$ - 723 K, is reduced by water to a lower extent. The model proposed was fitted well with the experimental data.

Li et al. [15] studied a Lumped-Parameter model using Zn/ZSM-5 catalyst for the transformation of methanol to aromatics (MTA) (Figure 1). The kinetic model could accurately predict the distribution of light aromatics. The methanol conversion remained relatively constant as the catalyst activity reduced, but the W/F yield dramatically decreased, indicating that the W/F yield would appear to reduce with the activity of the catalyst.

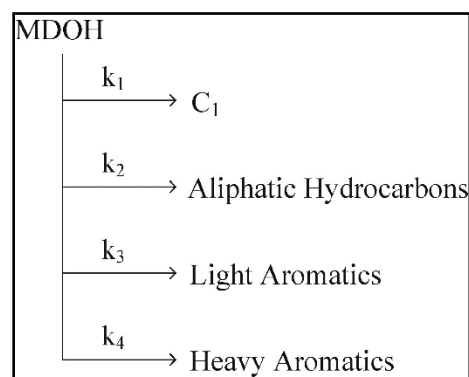


Figure No. 1: Catalytic route of MTA over Zn/ZSM-5 catalyst. Reprinted with permission from Ref. [15]. Copyright (2021) Elsevier.

The aromatic hydrocarbons were split into two parts: lower aromatics i.e., C_6 - C_8 , and higher aromatics i.e., C_9^+ for the prediction of the BTX yield. Alkanes, naphthenes, and olefins were all lump together as an aliphatic hydrocarbon. Methane, hydrogen, carbon monoxide, and carbon dioxide were lump as C_1 . With rising W/F, the transformation of methanol and yield of hydrocarbon enhanced. With increasing contact time, the gasoline yield was also increased, while the yield of lighter olefins reduced. The yield of DME and olefins was high at low conversion, but the yield of aromatics was negligible. The DME and lower olefins were partially converted to heavy hydrocarbons, which implies that methanol to hydrocarbon reactions produced intermediate products. The kinetic parameters of the deactivation model were estimated by simplex and non-linear least square method. The industrial data and the kinetic data were very well fitted, which can be used for future estimation of selective products and their compositions [15].

Lee et al. [2] proposed a modified Lumped-Parameter model for the transformation of methanol to olefins (MTO) using SAPO-34 catalyst in a fixed bed reactor. The products procured in this model were divided into 7 categories namely CH_4 , C_2 , C_3 , butene (C_4), C_3H_6 , C_4H_8 , and rest C_5^+ (Figure 2). Both reaction steps were assumed to be first-order, and the reduction of catalyst was corresponding to the transformation in the model. Oxygenates quickly reached equilibrium and were treated as a single group defined as MDOH. The primary product of MDOH was defined as all hydrocarbons produced using the SAPO-34. Since the experimental data used to be used in kinetic modeling was having minimal coke content, so the generation of coke was not involved in the model.

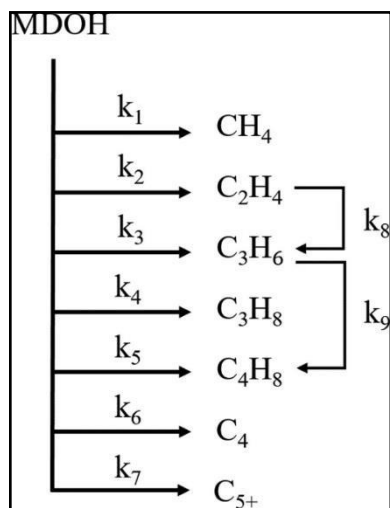


Figure No. 2: Reaction network of olefins process using SAPO-34 catalyst. Reprinted with permission from Ref. [2]. Copyright (2021) American Chemical Society.

To investigate the effects of catalyst activity on product distribution under various process conditions, a Lumped-Parameter model with nine reactions. The following two observations were used to support this: (1) the transformation versus contact time acquired from the test showed a common example of the 1st order reaction, and (2) the basic contact time acquired from 50% transformation of methanol versus contact time has a minimal value when contrasted with the related contact time [2].

Heriyanto et al. [1] developed a new Lumped-Parameter model for the methanol transformation to hydrocarbons (MTH) using a Ca-ZSM 5 catalyst. The effect of the kinetics of the reaction, as well as that of the temperature and weight hourly space velocity (WHSV) in the MTH process, was described using Lumped-Parameter models. These models were used to find out the optimal conditions for MTH conversion to accomplish maximum efficiency for olefin production. The Lumped-Parameter models had clarified the conduct of the kinetics of the reaction and the impact of the temperature and WHSV in the process of MTH. These models were utilized to foresee the proper conditions to accomplish ideal olefin generation in the MTH process.

A Lumped-Parameter model mechanism was explained (Figure 3(a)), namely oxygenates, olefins, C_5^+ , and paraffins. In the fixed bed reactor, the reaction rate was thought to be power-law relations for determining kinetic parameters. An eight Lumped-Parameter model mechanism was explained (Figure 3(b)), including $C^=$ as 1, $C^=$ as 2 and 7, $C^=$ as 3 and 8, $C-C$ ($CH_4, C_2H_6, C_3H_8, C_4H_{10}$), and C^+ ($CH_5^+, C_2H_7^+, C_3H_9^+, C_4H_{11}^+$) as 4, C^+ ($CH_5^+, C_2H_7^+, C_3H_9^+, C_4H_{11}^+$) as 5, DME as 6, and coke as 9 were included in the model. Coke was terminated because kinetic data were collected at a low TOS, allowing the coke generation to be overlooked. The grouped component, as well as the gas analysis results in the fixed bed reactor's product outlet, were used in kinetic modeling [1].

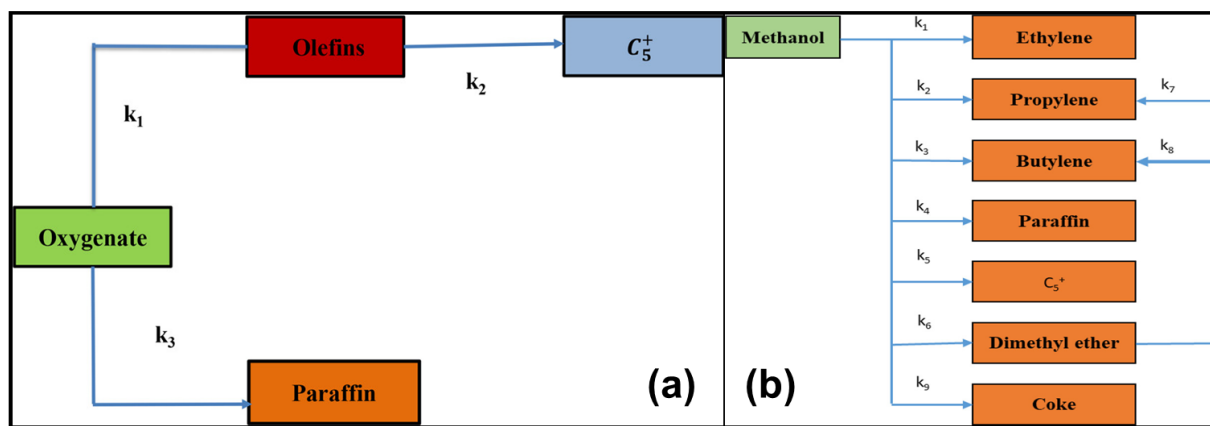


Figure No. 3: Kinetic model mechanism (a) Four Lumped-Parameter model, (b) Eight Lumped-Parameter model. Reprinted with permission from Ref. [1]. Copyright (2021) American Chemical Society.

A Lumped-Parameter model shows the value of the rate constant in increasing order of k_1 (344.6 h^{-1}) > k_3 (156.7 h^{-1}) > k_2 (29.3 h^{-1}). As a result, the olefin reaction rate was quicker than that of paraffins and C_5^+ . A Lumped-Parameter model revealed that k_7 (1181 h^{-1}) > k_8 (419.8 h^{-1}) > k_3 (31.6 h^{-1}) > k_1 (3.9 h^{-1}) > k_4 (3.5 h^{-1}) > k_5 (3.43 h^{-1}) > k_6 (2.9 h^{-1}) > k_2 (0.1 h^{-1}). Propylene's rate constant of 1181.1 h^{-1} (sum of k_2 and k_7), and its $E_a = 109.3 \text{ kJ mol}^{-1}$, was higher as compared with the rest. Lower olefins had a higher weight fraction than the other products. Surprisingly, the transformation of methanol to propylene was lower in the model as compared to the DME to propylene. This demonstrated that DME generated by dehydration of methanol could be transformed into propylene much efficiently on the Ca-ZSM-5 catalyst [1].

III. Kinetic modeling of ethanol to hydrocarbons

(a) Langmuir-Hinshelwood model

Becerra et al. [10] proposed an applied plan of an industrial plant for delivering ethylene from aqueous bioethanol over HZMS-5 catalysts and developed a kinetic model for ethylene production (Eq. 16) following Arrhenius model (Eq. 17):



$$-r_A = K_0 e^{\frac{-E_a}{RT}} [P_i] \quad (17)$$



$$r_A = \frac{k_1 P_A - k_2 P_E P_W}{(k_2 + P_A K + P_E)} \quad (21)$$

where A = ethanol, S = catalyst surface, F.S = species formed to the catalysts surface after ethanol adhered; E = Ethylene; W = Water; P_A = Ethanol partial pressure (atm/atm); P_W = water partial pressure, P_E = Partial pressure of ethylene (atm/atm), r_A = reaction rate ($\text{mol s}^{-1} \text{g}^{-1}$), and k, k_1, k_2, k_3 = reaction rate constant ($\text{mol s}^{-1} \text{g}^{-1}$).

The adsorption, surface, and desorption reaction occurred over the surface of the catalyst by using the Lumped-Hinshelwood method, mentioned in Eq. 18-19 which stated the rate-limiting reaction for the model. The model based on the Lumped-Hinshelwood method was developed at $T = 473\text{-}573 \text{ K}$ range with $E_a = 14 \text{ kJ/mol}$ [10].

(b) Lumped parameter model

Aguayo et al. [16] studied the aqueous transformation of ethanol to hydrocarbons using HZSM-5 catalyst and aimed to reduce the water's impact. Step-1 of the scheme corresponded to ethanol dehydration. Step-2 corresponds to an oligomerization-cracking reaction. Here, ethene was the reactant and products were lower olefins ($\text{C}_3^=$ and $\text{C}_2^=$). The oligomerization-cracking-aromatization of ethane produced hydrocarbons of lump C_5^+ i.e., gasoline (Step-3). The C_5^+ was also procured by condensation of olefins (Step-4). Cracking of the C_5^+ provided ethene and olefins (Step-7). Paraffins were obtained as a result of the ethene oligomerization-cracking (Step-5) and cracking of the C_5^+ (Step-6).

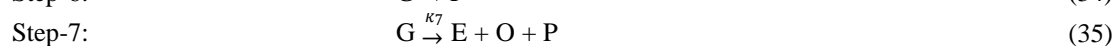
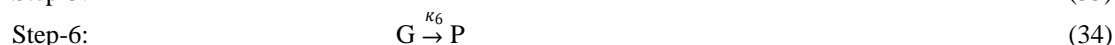


where E, G, O, P represents the $\text{C}_2^=$, the lump of gasoline (C_5^+), the lump of $\text{C}_3^= + \text{C}_4^=$, and the lump of lower paraffins (C_4), respectively; k_i = kinetic constant of i^{th} species, h^{-1} .

This kinetic model was proposed at $T = 623\text{-}723 \text{ K}$ based on experiments performed in a fixed-bed reactor. As the W/F in the catalyst bed increased at $T = 573 \text{ K}$, the amount of coke over the catalyst increased. The increase

in olefins and gasoline amount in the reaction medium explains this rise, which becomes less noticeable as there is an increase in the amount of water in the reaction. Maximum coke deposition was identified at $T = 673$ K, which can be described by coke precursor oligomer cracking above this temperature. At $T = 723$ K, the impact of water concentration in the reaction on reducing the coke deposition followed the same pattern. However, the impact of W/F was more complicated, and the amount of coke in the catalyst bed reached a limit, which is clarified by the breakdown of coke precursors above a certain W/F value. It was also discovered that the global process economy (stage-1, partial water removal; stage-2, catalytic transformation) entailed minimizing the requirements of stage-1 and taking into account the reduction in stage-2 because of the availability of water in the reaction [16].

Gayubo et al. [17] proposed a Lumped-Parameter model for the transformation of bioethanol to hydrocarbons using a catalyst low coke formation. The kinetic modeling process included the subsequent steps: (i) proposing the alternatives for the kinetic model, (ii) model resolution and estimation of the kinetically excellent fitting of parameters, and (iii) model differentiation.



where E, G, O, P represents the $C_2^=$, the lump of gasoline (C_4 and C^+), the lump of $C^= + C_3^=$, and the lump of lower paraffins (C_4), respectively; $k_i^=$ = kinetic constant of the i^{th} species, h^{-1} .

The following variations from Aguayo et al. [21] were considered: (i) during the generation of propylene and butene a new autocatalytic step is examined (Step-2), (ii) The heavier hydrocarbons were formed due to the combination and reaction of ethylene and the lump of lower olefins (Step-4), (iii) The reduction of the water in the reaction was included for all kinetic scheme. For an HZSM-5 catalyst having modifications using NaOH, the kinetic model was developed for measuring the lump of product distribution at a time ($t = 0$) in transforming the bioethanol under a broad range of working situations ($T = 573$ - 673 K). This modification was successful in reducing the coke deactivation. The kinetic model was especially useful for calculating the concentration of the propylene + butene lump. For W/F values greater than $0.6 h^{-1}$ and critical operating constraints for catalyst durability ($T = 648$ K and more amount of water in ethanol, 75 wt%), the highest concentration and generation rate was obtained [17].

Gayubo et al. [18] proposed a Lumped-Parameter model for converting bioethanol into hydrocarbons using HZSM-5 catalyst doped with 1wt% Ni at $T = 673$ - 773 K which is necessary for achieving a maximum propylene and butene yield. This model was based on findings reported by Aguayo et al. [21] for a catalyst synthesized with an unmodified HZSM-5 catalyst that was only valid in the $T = 623$ - 723 K range due to the catalyst's hydrothermal instability at higher temperatures. Since temperatures above $T = 723$ K are needed to optimize propylene and butene yields, the generation of ethylene through reactions such as cracking involving lump of gasoline (C_4 and $C_5 - C_{12}$) becomes important, requiring consideration of Step 6 (Figure 4).

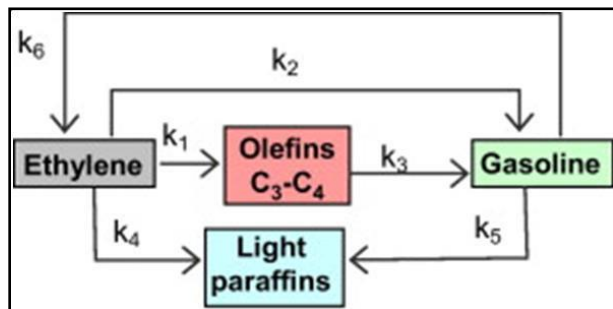


Figure No. 4: Reaction pathway for the bioethanol transformation into hydrocarbons at $T = 673\text{--}773$ K range. The terms E, G, O, P represents the C_3 , a lump of gasoline (C_4 and C^+ hydrocarbons), a lump of C^+ and C^- , and a lump of lower paraffins (C_4^+), respectively; k_j = kinetic constant of j species, h^{-1} . Reprinted with permission from Ref. [18]. Copyright (2021) Elsevier.

The reaction steps were described in Figure 4. The proposed kinetic model for the reaction helps in the quantification of product distribution in the form of a lump at $T = 673\text{--}773$ K and under varying W/F and amount of water in the feed). The breakdown of higher hydrocarbon lump, as well as the reducing impact of water in the reaction, affected all the steps leaving only the ethanol dehydration step. The 2nd order for transforming ethylene into C_3 – C_4 olefins and the gasoline lump should need to be taken into account in the model. To create the optimized conditions for a good C_3 and C_4 yield, the model quantified the number of water effects in the reaction, which reduced the reaction steps in the kinetic scheme and coke deactivation.

IV. Conclusions

Due to the scarcity of available non-renewable resources, scientists have been encouraged to advance present technology to manufacture the chemicals using viable resources in a better environmentally friendly way. One of the productions of the interesting alternative of lower olefins and higher carbon chain hydrocarbons from methanol and ethanol.

Kinetic modeling aids researchers in interpreting the mechanism of a catalytic reaction and simulating experimental effects. The Lumped-Parameter parameter model reduces difficulty by assembling components into a form of lumps having indistinguishable properties and modifying the reaction pathway among them. As a result, the Lumped-Parameter parameter model has the benefits of less computation performed for the evaluation of parameters and is easy to apply to reactor design. Langmuir-Hinshelwood model is the broadly used kinetic expression to describe the kinetics of the heterogeneous catalytic processes but Lumped-Hinshelwood kinetics to zero-order kinetics is both impossible and inappropriate.

However, the catalyst's efficiency needs to be enhanced even more to minimize coke, and secondary reactions to aromatic and paraffin.

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