

# Study on kinetic model of microwave thermocatalytic treatment of biomass tar model compound

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## **Study on kinetic model of microwave thermocatalytic treatment of biomass tar model compound**

### **Abstract**

Kinetic model parameters for toluene conversion under microwave thermocatalytic treatment were evaluated. The kinetic rate constants were determined using integral method based on experimental data and coupled with Arrhenius equation for obtaining the activation energies and pre-exponential factors. The model provides a good agreement with the experimental data. The kinetic model was also validated with standard error of 3% on average. The extrapolation of the model showed a reasonable trend to predict toluene conversion and product yield both in thermal and catalytic treatments. Under microwave irradiation, activation energy of toluene conversion was lower in the range of 3-27 kJ mol<sup>-1</sup> compared to those of conventional heating reported in the literatures. The overall reaction rate was six times higher compared to conventional heating. As a whole, the kinetic model works better for tar model removal in the absence of gas reforming within a level of reliability demonstrated in this study.

Keywords: Kinetic model; Microwave irradiation; Thermocatalytic treatment; Tar conversion; Toluene; Biomass gasification

### **1. Introduction**

Although biomass gasification offers a number of advantages compared to combustion process, the raw gaseous product contains not only combustible gases but also significant amount of fine particulates and tar. The latter products especially tar can cause severe problems associated with tar condensation that can clog downstream

equipment and detrimental to the internal combustion engine, gas turbine and fuel cell applications. Therefore, tar and also particulates must be eliminated to meet the requirement of end users.

In a number of experimental works, tar removal from producer gas by thermal and catalytic (thermocatalytic) treatment methods has been demonstrated. The related information of the methods has been extensively reported in several review papers. Besides real tar from pyrolysis or gasification of solid hydrocarbons, the capability of this method has also been performed for tar model compounds reduction. Toluene has been found as one of the most frequently used tar model compounds in the literatures. In common, tar model removal is conducted in electrical heating reactor under various parameters including reforming agents, catalysts, pressures, reaction temperatures and residence times. In this case, thermal stability of tar model compounds that determine the rate of conversion reactions depends on several parameters i.e.: (1) the strength of the weakest bond; (2) the number of weak bonds; (3) the size of the molecule; (4) the possibility of an intra-molecular H-shift or another rearrangement reaction leading to a less stable intermediate; (5) steric interactions in the molecule; and (6) the energy level of the radicals to be formed. In many cases, the first parameter is considered to be very important where the conversion kinetics of tar model can be predicted by the strengths of the bond broken in the radical-forming reaction. Another important parameter of thermal stability of tar is also their ability to form soot/coke which increases with unsaturation degree, molecular weight and aromaticity. Temperature, pressure and/or residence time are considered to be the key factors for radical formation. The presence of catalysts and reforming agents (steam,  $H_2$ ,  $O_2$  and  $CO_2$ ) then enhances tar conversion

at low temperature and determines what the products are formed, respectively. It was found that steam and  $H_2$  also improve the rate of toluene conversion.

Regardless of the above parameters, it should be noted that the heating strategy plays an important role during tar conversion process as the reaction takes place at high enough temperature that requires a continuous supply of heat. In general, tar conversion reaction can be limited within a conventionally/electrically heated reactor due to the heat/mass transfer limitations as the heat is supplied from the external wall in most of the conventional heating reactors. It is believed that the heating strategy by means of microwave irradiation which offers various advantages can solve the limitations of conventional heating. The unique feature of volumetric heating of this technique can result in more rapid heating process of the reactor in the presence of absorber material, thereby saving energy significantly, reduce process time, improve process yield, and environmentally friendly. In this sense, the use of microwave energy for thermocatalytic treatment of toluene as tar model compound has been investigated. This strategy was found to be a very attractive technique for toluene conversion which is not only effective but has also low energy consumption. Regarding gas phase reactions, microwave irradiation helps in triggering radicals formation making it possible to accelerate the reaction, save space and provide better energy utilization on reactants.

One of the most important tasks is to evaluate the kinetic parameters for tar decomposition reactions. To date, a number of works on kinetic model of toluene conversion have been performed to predict the experimental data that mostly obtained from conventional heating reactor. However, because the heating strategy using microwave irradiation could affect toluene conversion as previously elucidated, a kinetic model should also be determined for interpreting the experimental observations.

This evaluation essentially assists in designing the reactor, optimizing the operating conditions and predicting the reaction behavior. The current paper focused on the kinetic model of tar model compound (toluene) conversion by thermal and catalytic treatments using Y-zeolite and dolomite under microwave irradiation. The kinetic parameters of each product yields were also evaluated. In addition, coke/soot reduction activity was introduced and incorporated into the kinetic model. The kinetic model was validated and evaluated critically by comparing the results to published experimental results of conventional heating to assess the effect of microwave thermocatalytic treatment on toluene conversion under nitrogen stream. The kinetic parameters were reevaluated at a fixed pre-exponential factor and temperature to give a simple quantitative comparison of activation energy.

## **2. Experimental data**

Published experimental data on thermocatalytic treatment of toluene as a biomass tar model compound under nitrogen stream was acquired in a microwave tar treatment reactor. Toluene was cracked by means of both thermal and catalytic treatments operated at temperatures and residence times in the range of 450-1050°C and 0.24-0.5 s, respectively. Two types of catalyst namely Y-zeolite and dolomite were employed in the study and details of the experiments are given in the previous paper. The reaction conditions are summarized in Table 1.

Essentially all available data in this literature were considered for evaluating the kinetic model. Nevertheless, the experimental results obtained were modified and rearranged to simplify the kinetic analysis, in which the yields of light hydrocarbons (HCs) such as CH<sub>4</sub>, C<sub>2</sub>H<sub>x</sub> and C<sub>6</sub>H<sub>6</sub> were lumped together as yield of hydrocarbons.

Therefore, the products from toluene conversion were divided into three primary products that are coke/soot, hydrocarbons (HCs), and hydrogen (H<sub>2</sub>).

### *2.1 Kinetic modelling*

In many cases such as in the hydrocarbons combustion processes, the residence time is very short, within a few milliseconds only. During the process, soot formation in general was observed at a residence time of about 0.5 ms and reached a maximum value at around 2 ms. Recently study showed that the final step in the soot formation process had a residence time of 4 ms. Meanwhile, in other cases such as in the hydrocarbons or biomass gasification/pyrolysis processes, the residence time is relatively longer (usually more than 100 ms). In this work, the residence time in the hot zone ranging from 125 ms to 200 ms. At these conditions the soot is supposed to be completely formed.

Moreover, although toluene decomposition in the absence of reforming agents usually occurs in chain reaction where the radicals are formed in the first reaction, the radicals rates of change after a very short time can be never be great because they are present in such small quantities. Hence, coke/soot product can be assumed to be formed in a single step reaction as given in Eq. (4).

Based on the experimental results, the kinetic model of toluene conversion under thermal and catalytic treatments was developed and the reaction mechanism is given in Fig. 1. This mechanism is preferred to explain the main products formation during toluene conversion. Moreover, the mechanism also obey the general cracking reaction of toluene in the absence of reforming agents as expressed below:

Based on Eq. (1), there are several possible reactions for products formation that can occur during toluene decomposition i.e.:

It is generally agreed that toluene decomposition usually occurs in chain reaction where the radicals are formed in a first reaction. The radicals then react with toluene to form products and more radicals in several propagation steps.

The model presented in this study includes a number of assumptions as follow:

- a. Assuming pseudo-steady state for the radicals because they are present in such small quantities and in a very short time. Thus, the biomass tar model compound (toluene) is assumed to be converted according to single three parallel reactions step, yielding  $H_2$ , HCs and soot/coke,
- b. Perfect plug flow of the gas phase,
- c. Isothermal conditions and steady state operation (i.e. no gas accumulation in the bed), and
- d. Negligible increase in gas flow due to products generation.

Assuming first order kinetics for all processes, the reaction kinetics represented by the kinetic model illustrated in Fig. 1 can be expressed according to the following equations:

- a. Global kinetic of toluene conversion

The disappearances or conversion rate of toluene under thermal and catalytic treatments using Y-zeolite and dolomite into other products are given by:

where the reaction rate constant,  $k = k_1 + k_2 + k_3$  and  $F_T$  is the mass of the remaining condensed tar.

For  $n = 1$ , Eq. (5) can be integrated with initial condition of  $F_T(0) = F_{T,0}$  (initial mass of tar model) to give the tar content:

It is of interest to define the reaction rate in term of tar conversion ( $X_T$ ) instead of tar content to obtain the following expression:

where  $X_T$  is defined as:

By rearranging Eq. (7), the reaction rate constant at a particular residence time ( $t$ ) can be expressed as follows:

For  $n \neq 1$ , after integrating of Eq. (5), the following expression of the reaction rate constant is obtained:

It is assumed that the reaction rate constant changes with absolute temperature according to the Arrhenius equation. This model is used almost universally to express the temperature dependence of the reaction rate constant and is defined as:

where  $k_0$  is the pre-exponential factor ( $\text{s}^{-1}$ ),  $E$  is the activation energy ( $\text{kJ mol}^{-1}$ ),  $R$  is universal gas constant ( $0.008314 \text{ kJ mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is reaction temperature (K).

By substituting Eq. (9) or Eq. (10) into Eq. (11), the following expressions are obtained:

The plot of  $\ln \left[ \frac{-\ln(1-X_T)}{t} \right]$  vs  $\frac{1}{T}$  or  $\ln \left[ \frac{(1-X_T)^{1-n}-1}{(n-1)tF_{T,0}^{n-1}} \right]$  vs  $\frac{1}{T}$  is a straight line with slope equal to  $-\frac{E}{R}$  and an intercept equal to  $\ln(k_0)$ .

#### b. Kinetic model of products formation

In principle, the reaction rate constants of the three reactions ( $k_1$ ,  $k_2$  and  $k_3$ ) can be determined by measuring the amount of each product under investigated condition. Assuming that each reaction is first order, the formation rate of each component is given by:

where  $F_H$ ,  $F_O$  and  $F_S$  represent the hydrogen, HCs and soot/coke contents, respectively.

The solutions of Eq. (14-16) under the initial conditions of  $F_H(0) = F_O(0) = F_S(0) = 0$  are:

Eq. (17-19) can also be expressed in term of mass fraction ( $X_H$ ,  $X_O$  and  $X_S$ ) by dividing them by the initial amount of tar to obtain the relationships as follow:



The assumption of  $n = 1$  with respect to tar model might be revised in the future in order to obtain the best fit for the kinetic model. Nevertheless,  $n = 1$  was selected in this work as generally assumed in other studies.

### **3. Result and discussion**

#### *3.1 Global kinetic of toluene conversion*

In point of fact, tar decomposition reactions are very complex, usually chain reaction mechanism includes multiple, parallel and series reactions occurred during initiation, propagation and termination stages. So the reaction kinetic presented in Fig. 1 is a simplified approach to assess the main reactions. In this study the reaction rate of toluene conversion by means of catalytic and thermal treatment is related mainly to temperature and residence time.

Fig. 2 shows Arrhenius plot of reaction rate constants for each treatment method that is thermal and catalytic treatments using Y-zeolite and dolomite catalysts. In general, the Arrhenius plot of each treatment gives a straight line with a coefficient of determination ( $R^2$ ) of more than 0.95 on average. As shown, the highest and the lowest slopes of the trend lines were obtained by thermal and Y-zeolite catalytic treatments, respectively. It is understood that a tar treatment process with a steep slope of the trend line indicating the process requires high activation energy. Based on transition state theory, the activation energy ( $E$ ) is defined as the difference between the average energy of molecules undergoing reaction and average energy of all reactant molecules. On the other hand, the frequency factor/pre-exponential factor represents a measure of the frequency at which all molecular collisions occur regardless of their energy level. Thus the reaction rate constant is directly related to the catalyst and thermal activity and the tar reactivity to be destroyed.

The resulting kinetic parameters from the slope of the data for all treatment methods are given in Table 2. It was found that the lower activation energy value of Y-zeolite than dolomite catalyst and also thermal treatment process indicated that it is more active for toluene conversion. It is possible that the vaporize toluene is adsorbed on the active sites of Y-zeolite particles and undergoes cracking and polymerization reactions. Moreover, Y-zeolite catalyzes the formation of radical compounds that take part in heavy hydrocarbon polymerization reactions, while the reaction products were deposited as coke on the surface of the catalyst. The higher catalytic activity of Y-zeolite is then attributed to its acidic nature and higher surface area that supports removal of toluene.

The experimental values for thermocatalytic treatment of toluene conversion and the corresponding results from the predicted model at different temperatures are shown in Fig. 3. The predicted toluene conversion efficiency of each treatment method was calculated based on data available in Table 2. As shown, generally all the predicted models of toluene conversion efficiency under thermal and catalytic treatments using Y-zeolite and dolomite agreed well with the experimental results. Furthermore, conversion efficiencies calculated by extrapolation of the models indicate a reasonable trend. Fig. 3 shows that at temperatures of more than 1000°C, toluene conversion efficiencies obtained by the three different treatment methods offer almost similar conversion values. It means that at very high reaction temperature, the presence of catalysts is not important. In this condition, the reaction temperature plays a significant role that determines the rate of toluene conversion.

### 3.2 Kinetic model of products formation

As a consequence of the parallel reaction mechanism used in this paper, the products formations fall into competitive reaction conditions. Experimental results from thermocatalytic treatment of toluene especially from catalytic treatment processes showed that coke/soot formation tends to decrease at certain reaction temperature. Thus, in order to accommodate this behavior, the coke/soot reduction activity function ( $I$ ) was introduced and incorporated into the soot reaction rate ( $r_s$ ) to obtain the best fit for the kinetic models. So that Eq. (16) becomes:

In this case, the soot reduction activity is defined as:

where  $\alpha$  is the reduction activity constant.

With substituting Eq. (24) into Eq. (23) and then integrated with initial conditions of  $F_s(0) = 0$ , the following expressions are obtained:

At the condition where soot formation increases with the increase of temperature, the reduction activity constant ( $\alpha$ ) is equal to zero and the soot reduction activity function becomes unity. Therefore, Eq. (25) and (26) will then similar to Eq. (19) and (22), respectively.

The maximum theoretical soot yield or ultimate soot yield can be defined as: which substituted into Eq. (26) yields:

As there is in the reaction rate constant ( $k$ ), the reduction activity constant ( $\alpha$ ) is also assumed to follow an Arrhenius law. So that, where  $\alpha_0$  is the pre-exponential factor of soot reduction activity.

The plot of  $\ln(\alpha)$  vs  $\frac{1}{T}$  is a straight line with slope equal to  $-\frac{E}{R}$  and an intercept equal to  $\ln(\alpha_0)$ .

The kinetic parameters of the three parallel reaction models from catalytic and thermal treatment processes are estimated based on Arrhenius law as shown in Eq. (12) and (29) and listed in Table 3. As shown, the activation energy and pre-exponential factor of hydrogen formation provided from Y-zeolite catalytic treatment of toluene are higher than that of other products (excluded soot reduction). While the activation energy and pre-exponential factor of hydrocarbons are the lowest. These results give a clear description that hydrocarbons formation is more favorable than that of hydrogen during toluene conversion using Y-zeolite catalyst. Different results were obtained in catalytic treatment using dolomite and thermal treatment. These methods tend to form hydrogen as an important gas product.

The prediction of products evolution is a crucial factor for the proposed kinetics model. This model can be applied to predict the yields of products in a wide range operating conditions. Fig. 4 shows the comparison of products yields calculated by the model with experimental results of toluene conversion using Y-zeolite catalyst, dolomite catalyst and thermal treatment, respectively. In general, the calculated models predict the experimental yields of products very well, although slight under prediction was observed for the soot yield at around 650°C in the case of dolomite as shown in Fig. 4(b). Slightly under and over predictions were also observed for the hydrocarbons yield at temperature of 900-1000°C and above 1000°C, respectively in the case of thermal treatment as depicted in Fig. 4(c). The little difference between the predicted and experimental yields of hydrocarbons is attributed to the reduction of one or more component due to competitive reaction or might also be due to secondary reaction that is excitably occur at higher reaction temperatures. As mentioned before, this lump is a combination of light hydrocarbons including  $\text{CH}_4$ ,  $\text{C}_2\text{H}_x$  and  $\text{C}_6\text{H}_6$ . This explanation is

supported by the results demonstrated in previous study which showed that  $C_{2+}$  hydrocarbons yield start to decrease at temperature of about 950°C.

The extrapolation of the fitting kinetic models is also point out in Fig. 4. The products yields calculated by the model at both lower and higher temperatures than experimental temperatures provide a very considerable trend. However, the extrapolation of the fitting models is limited at certain temperatures. The results showed that temperature up to 900°C is appropriate and acceptable to predict the yields of products by extrapolation in both Y-zeolite and dolomite catalytic treatments. Whilst for thermal treatment, it was calculated that temperature up to 1100°C is still reasonable.

### 3.3 Validation of the kinetic model

The estimated parameters of the kinetic model obtained above need to be verified whether the kinetic model meets the experimental data. The evaluation of the kinetic model that best fits the data was accomplished by comparing the standard deviations of the fitted parameters and the sums of squares. From the latter, the standard error of the estimate (*SEE*) or the combined residual variance was calculated as: where  $F_{exp,i}$  and  $F_{mod,i}$  represent the yields of products obtained by experimental and estimated by the model for each treatment methods, respectively.

The experimental versus predicted yields of products from thermocatalytic treatment of toluene are given in Fig. 5. As shown, all the predicted yields data by the kinetic model give accurate predictions, although there were some data points at which the predicted yield differed slightly from experimental data especially organic HCs and condensed products in thermal treatment process. The  $R^2$  was 0.97 indicating the predicted data was in agreement with the experimental data. The results showed that the *SSE* of each treatment methods for toluene conversion with two degree of freedom are

1.8%, 3.2% and 5.4% for Y-zeolite, dolomite and thermal treatments, respectively. In general, the average of *SSE* is about 3% indicating that the kinetic model predicts the experimental data very well and that the predicted values are reliable.

### *3.4 Comparison of kinetic model*

In the model presented before, the kinetic parameters  $k_0$ ,  $\alpha_0$  and  $E$  are highly correlated with toluene conversion data under experimental investigated conditions. Thus, comparison of these results with the kinetic parameters obtained in other studies is important. For this purpose, the overall reaction rate constant and thus the activation energy of each treatment process under microwave energy were used for comparison. However, there are some difficulties to compare the kinetic parameters directly including the different representations of residence time, the kinetic constants were evaluated under variety of mass transfer limitations, the different experimental apparatus and reforming agents.

In order to simplify the comparison of the kinetic models of toluene conversion, the obtained kinetic parameters in this study and also from other references used for comparison were recalculated at a fixed pre-exponential factor and temperature. Thus, the activation energy was the only fitting parameter. This approach has been found to be a good way for quantitative evaluation of activation energy using Arrhenius equation. Regardless of several difficulties as stated before, the pre-exponential factor for toluene conversion of  $3.16 \times 10^{15} \text{ s}^{-1}$  is preferred that estimated from the kinetic theory collision frequencies. The results of this approach are given in Table 4. The temperatures for recalculation of activation energy were respectively 700°C and 850°C for catalytic and thermal treatments. As shown, the activation energy found in this way becomes easier to

be compared. The obtained activation energies are in the ranges of 346-373 kJ mol<sup>-1</sup> for thermal treatment and 233-309 kJ mol<sup>-1</sup> for catalytic treatment.

The result shows that the activation energy in thermal treatment is about 3-27 kJ mol<sup>-1</sup> lower than that of other studies. In catalytic treatment, the activation energy provided from dolomite is also lower in the ranges of 16-25 kJ mol<sup>-1</sup> than that of other natural basic mineral catalysts found in the literatures. The low activation energy compensates the acceleration of toluene conversion. However, compared with nickel-based catalysts, the activity of both Y-zeolite and dolomite are much higher in order 39-49 kJ mol<sup>-1</sup>. This is not surprising because the nickel-based catalysts have been widely known to have a high tar conversion activity.

To get a better overview about the observed acceleration of toluene conversion rate under conditions investigated, the recalculated kinetic parameters are employed to predict the residence time required at a given temperature to arrive at a particular conversion rate. The result is depicted in Fig. 6. It can be seen from this figure that almost complete conversion of toluene required a residence time of about 1 s and 4 s for Y-zeolite and dolomite, respectively. For thermal treatment, it needed 25 s of residence time which is about six times faster on average compared to other studies.

There are several possible reasons regarding the difference of activation energy obtained in both thermal and catalytic treatments particularly for dolomite with other literatures above. On the one side, this difference is caused by the differences of gas environment/carrier gas used. It is generally agreed that the presence of H<sub>2</sub>O and H<sub>2</sub> during thermal treatment of toluene increased the reaction rate by a reaction order of 0.5 whilst for catalytic treatment, their presence reduced the toluene conversion rate. On the other side, the differences of physical and chemical properties as well as the origin of

the catalysts are also attributed to the disparity of activation energy. These reasons are acceptable in the case of catalytic treatment; however it were not appropriate to explain the discrepancy of activation energy for thermal treatment. Thus, the main reason is due to the different heating strategy. As previously described microwave irradiation is expected to trigger the toluene conversion reaction by helping to supply such amount of free-radicals to start and sustain the reaction.

There are two origin of the enhancement of reaction rate that can affect the three variables ( $k$ ,  $k_0$  and  $E$ ) in Arrhenius equation under microwave irradiation: thermal effect and specific (non-thermal) effect. The latter term, however, is still a controversial matter. Some literature reviews concluded that no evidence for the existence of specific effect under precise controlled internal reaction temperature measurements mentioned that the thermal effects are also the microwave-specific effects because of the rapid and volumetric heating phenomena that cannot be obtained by conventional heating process.

Apart from the above issues arise from the experimental observation conditions, it is necessary to compare and analyze the experimental results with theoretical analysis or mathematical model from relevant literatures. In this matter, the study of Bhattacharya et al. is considered as the most relevant literature that give comprehensively theoretical comparison of microwave and conventional heating effect on the endothermic gas phase reaction. They concluded that microwave heating homogenizes the localized reaction of conventional heating and thus enhances the overall rate of reaction with the increase of diffusional limitations (Thiele modulus,  $\phi > 1$ ) and total amount absorbed power. In contrast, in kinetically controlled regime ( $\phi < 1$ ) there was no difference of the two heating modes.



Based on the above description, the enhancement of reaction rate by microwave energy is highly possibly in the case of thermal treatment process that normally takes place under diffusion controlled regime. Whilst in catalytic treatment process that normally occurs under reaction controlled regime, the enhancement of reaction rate is dominated by the ability of the catalyst activity. These factors are in accordance with the results in this study. Nevertheless, once coke/soot formed and deposited on catalyst surface, the reaction regime might be switched suddenly from reaction controlled into diffusion controlled regime. This process possibly occurs because the ability of coke to absorb microwave energy, thus improves the total amount absorbed power resulting in the high frequency vibration of molecule and motion energy, and thus, self-heating.

#### **4. Conclusion**

Kinetic models for toluene conversion under microwave thermocatalytic treatment are described by first-order reactions. The results show that the model is more suitable to predict the yield of products during decomposition of toluene. Moreover, the model predicts the experimental data very well with a standard error below 5%. It was found that the activation energies were lower under microwave heating compared to that of conventional heating mechanism. In thermal treatment process, the enhancement of reaction rate is highly affected by microwave irradiation whereas for catalytic treatment, this effect only plays a minor role.

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