Kinetics of Catalytic Carbon Dioxide Gasification of Refuse Plastic Fuel

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Abstract: Gasification is a waste-to-energy conversion process that involves the thermal degradation of the feedstock to produce synthesis gas. This study seeks to provide kinetic parameters of gas-solid kinetic models when applied to the carbon dioxide gasification of waste plastic feedstock, high-density polyethylene (HDPE) and polypropylene (PP), using potassium carbonate (K_2CO_3) as a catalyst. Gasification was performed in thermogravimetric analyzer with catalyst loading varied from 1 wt% to 5 wt%. The gasification reactions were out non-isothermally from room temperature to temperatures of 600, 700, 800 and 900°C. The gasification reactions were modeled using the volumetric model (VM), modified volumetric model (MVM), extended volumetric model (EMVM), the shrinking core model (SCM) and the random pore model (RPM). Among these models, the EMVM best fits the gasification of both HDPE and PP was determined to be the EMVM. The activation energies for the gasification reactions of HDPE and PP were observed to be 357.5 and 190.2 kJ/mol, respectively.

Key Words: HDPE; PP; gasification; gas-solid reaction model

1. INTRODUCTION

Plastic is known as a non-biodegradable product and is commonly used around the globe. Geyer, Jambeck, and Law (2017) reported that, of the 6,300 metric tons of plastic that has been generated from 1950 to 2015, approximately only 9% has been recycled, 12% incinerated, and the rest left to accumulate in landfills or the environment. A sustainable method to reduce the accumulation of this product in landfills is to use them as feedstock to recover its calorific value through gasification. This is a process requires high temperatures to decompose materials with high carbon content such as biomass, coal or plastics, to produce syngas along with light hydrocarbons like CH_4 and C_2H_6 and traces of higher chain hydrocarbons with some tar and char (Burra & Gupta, 2018). Furthermore, plastics have a higher heating value over cellulosic material from biomass which make it more suitable for energy recovery.

The gasification of plastics is difficult to perform due to the stable polymeric structure of plastics. The gasification process itself is slow due to the numerous reactions that occur simultaneously which includes the Boudouard reaction and water-gas reaction. Compounds of alkali metal catalysts are widely used to increase gasification reaction rates involving carbonaceous materials. Specifically, salts of potassium exhibits excellent performance as a catalyst at low loadings for the carbon dioxide gasification of biomass.

In this study, potassium carbonate was used as a catalyst in the CO_2 gasification of refuse plastic fuel. The catalyst was varied from 1 wt% - 5 wt% loading. The gasification reactions were modelled using the volumetric model (VM), modified volumetric model (MVM), extended volumetric model (EMVM), the shrinking core model (SCM) and the random pore model (RPM). Using the model that best fits the gasification reactions, the kinetic parameters were evaluated to determine the effect of the catalyst on the rate of the gasification reactions.

2. METHODOLOGY

The plastic samples were obtained from a plastic waste processing plant, where samples containing high-density polyethylene (HDPE) and polypropylene (PP) were extruded into pellet form. The average height of the pellet was 3 mm and diameter of 1 mm and weighing approximately 10 mg. The catalyst used was potassium carbonate which were loaded to the samples at 1 wt%, 3 wt%, and 5wt % loading via physical mixing.

The gasification of RPF was carried out non-isothermally using carbon dioxide as gasifying agent. Approximately 10 mg of the sample was loaded onto the platinum pan of the TGA and heated to 110 °C at a heating rate of 20 °C /min to remove any residual moisture.

As the temperature started to increase, gasification was carried out under an argon-carbon dioxide atmosphere. The composition of the gasifying agent was 60 vol% CO_2 + 40 vol% Ar to eliminate the inhibiting effect of carbon monoxide formed at concentrations above 60 vol% CO_2. The final temperature in the furnace was set to 600°C-900°C at 100°C interval at a heating rate of 20°C/min.

3. RESULTS AND DISCUSSION

The weight of HDPE was observed as the temperature increased in the thermogravimetric analyzer for the entire duration of each run. Results showed that the presence of catalyst generally increases both the initial and final gasification temperatures by approximately 10°C to 20°C. However, there was no trend observed between the increase in catalyst loading to the initial and final gasification temperature which was constantly between ranges of 454°C-466°C. The fractional weight was calculated and plotted against temperature as shown in **Figure 3.1**. These graphs further support that temperature range for the catalyzed gasification of HDPE are at higher temperatures than pure HDPE with the exception of runs performed with programmed temperature of 600°C. This is exhibited by the shift of the TG curve of the catalyzed runs to the right of the plot by 10°C to 20°C compared to uncatalyzed runs.
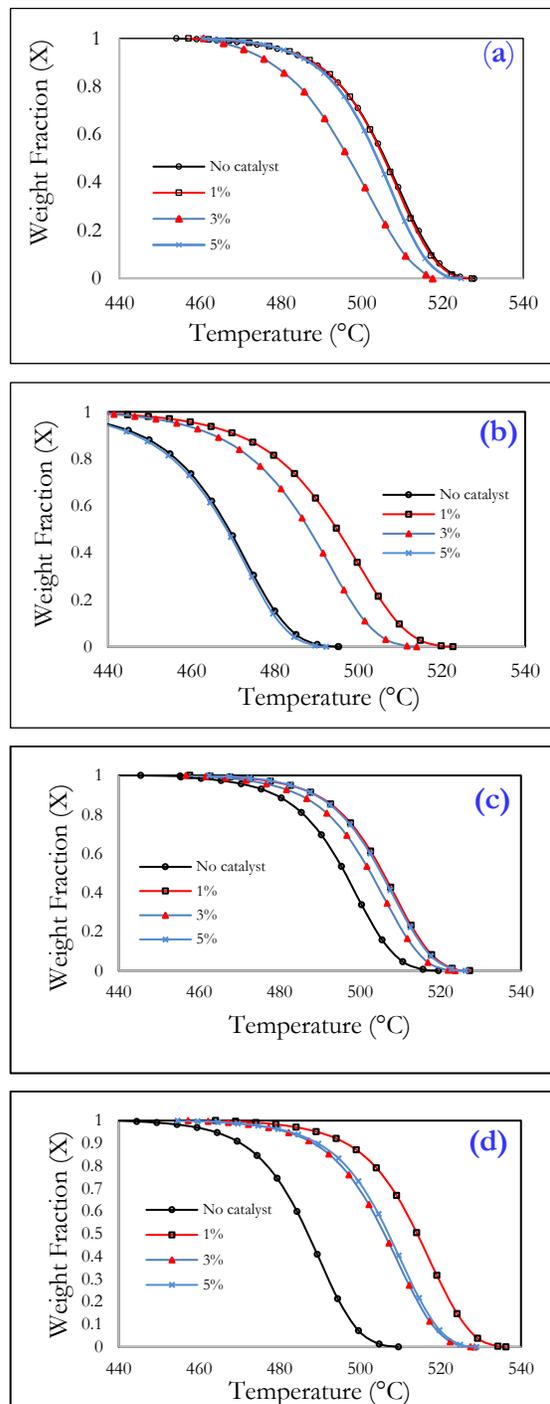
Figure 3.1 Weight fraction remaining vs temperature for HDPE at (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C.

Also on **Figure 3.1**, the K_2CO_3, beyond the addition of 1% loading, does not result in a significant effect in the rate of gasification. The uneven distribution of the catalyst on the sample surface may have contributed to the absence of an evident trend in the gasification of HDPE. The catalyst was unevenly distributed and present on only some sites on the surface of the samples, thus a uniform catalytic effect cannot be expected from the experiments. Unlike HDPE, the results of the PP samples show that the presence of the K_2CO_3 did not always result in the increase in initial and final gasification temperature. The fraction remained for the gasification of PP was plotted against temperature and is shown in **Figure 3.2**.

It was observed from the graphs that there were no trends that were noticeable. Hence, the K_2CO_3 is revealed to be ineffective for the gasification of PP. The increase in the end set temperature also did not have an effect on the behavior of the gasification of PP since the gasification range is only between 398°C to 544°C after which majority of the plastic would have already been gasified and any residual would be combusted.

The differential thermogravimetric data shows the relationship between the rates of the weight change of the sample plastic versus the temperature, where the peak of each curve represents the maximum gasification rate achieved per run. For the gasification of HDPE. The addition of the K_2CO_3 was observed to generally decrease the peak gasification rates while the corresponding temperature behaved similarly to that of the TG curves that shifted to the right, particularly between the uncatalyzed run and the runs performed at 1% and 5% catalyst loading. These results differ from Bouraoui et al. (2016) where the addition of the potassium based catalyst resulted in the increase of gasification rate. Furthermore, the method of introducing the catalyst for their study was impregnation, allowing a better dispersion for gasification reaction as opposed to the uneven dry mixing of the catalyst on the surface of the plastic. The data obtained at different catalyst loadings is illustrated in **Figure 3.3.**
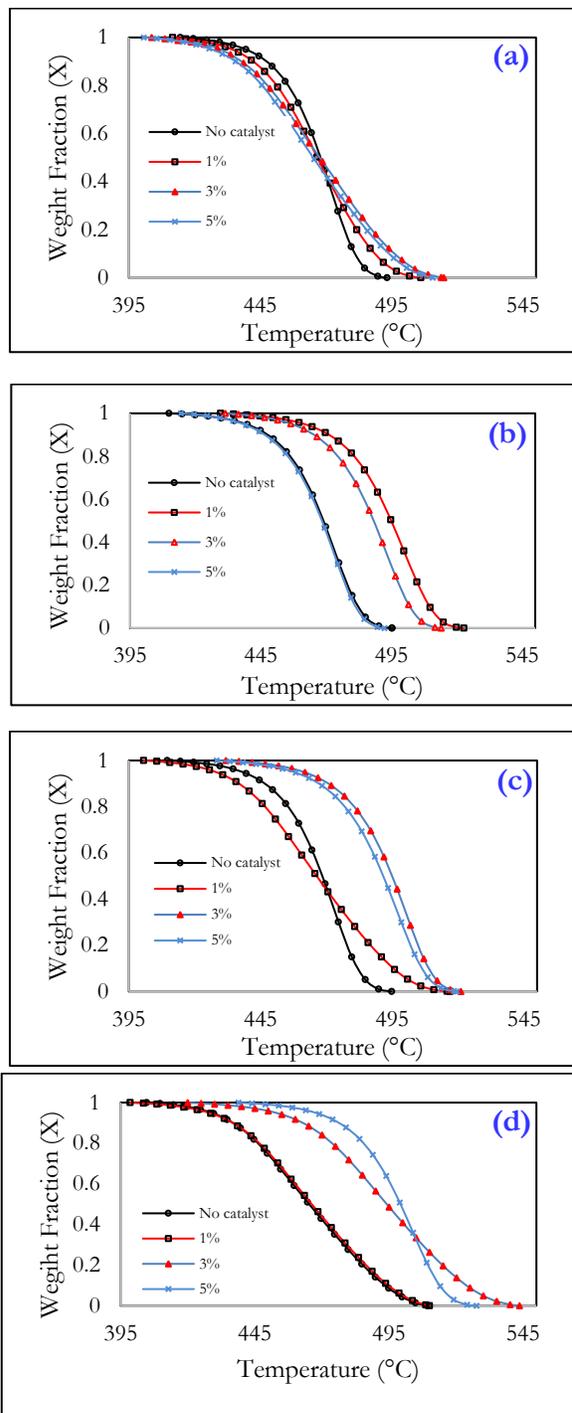
Figure 3.2 Weight fraction remaining vs temperature for PP at (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C.
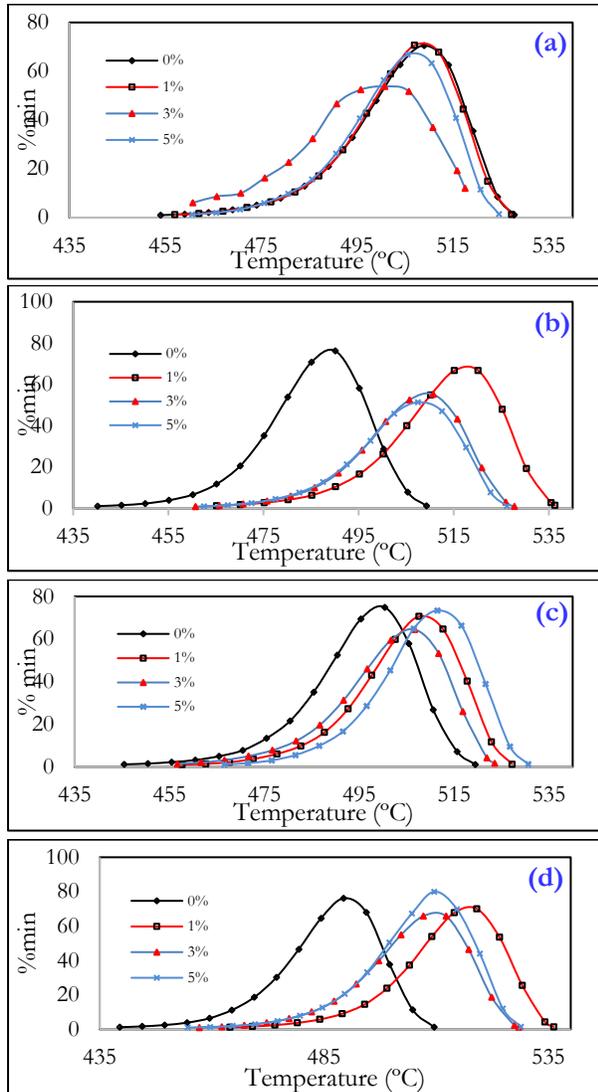
Figure 3.3 Rate of weight change vs. temperature of HDPE Sample with increasing catalyst loading at (a) 600°C, (b) 700°C, (c) 800°C and (d) 900°C.

Based on the statistics obtained from ANOVA tests, compared to uncatalyzed runs, there is a statistically significant increase in the peak gasification temperatures only at 1 and 3% catalyst loading.

The K_2CO_3 is observed to be ineffective for the gasification of PP. The increase in the set end temperature also did not have an effect on the behavior of the gasification of PP since the gasification range remained between 398°C to 544°C after which
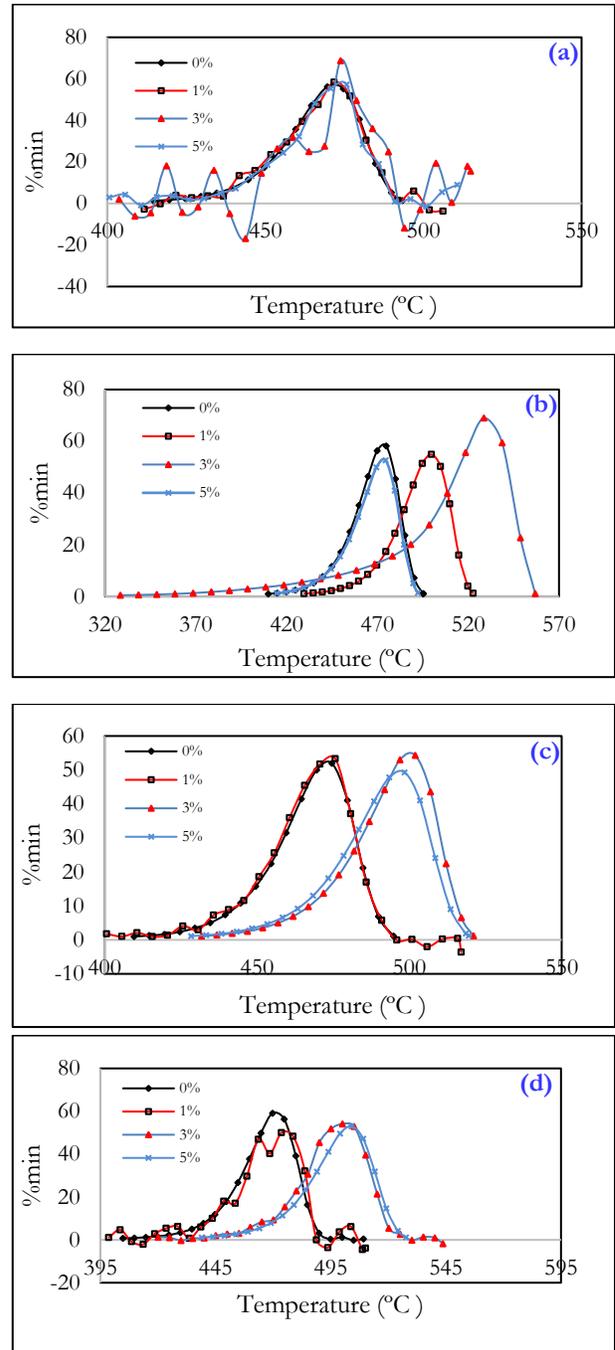
Figure 3.4 Rate of weight change vs. temperature of PP Sample with increasing catalyst loading at (a) 600°C, (b) 700°C, (c) 800°C and (d) 900°C.

the majority of the plastic had already been gasified and any residual combusted in the presence of air. There is no evident correlation between the catalyst loading and the maximum conversion rate of the sample. However, unlike HDPE, negative weight changes were observed for PP. This erratic behavior suggests that PP is more difficult to gasify than HDPE which may be attributed to the more complex repeating units than that of HDPE. The peak gasification temperatures of PP are generally lower than that of HDPE, similar to the study of Diaz Silvarrey and Phan (2016) on the thermal degradation of different plastics. The maximum gasification rate for each sample is illustrated in **Figure 3.4.**

The different models were tested using the experimental data for HDPE and PP to determine the applicability of each model. For the overall evaluation of the effectiveness of the models, EMVM was found to be most effective with coefficients of determination ranging from 0.9997 to 1.0. The order of effectiveness of the other models is MVM ≈ RPM > SCM > VM with VM having the lowest values of coefficients of determination at 0.8840-0.9429 for HDPE and 0.9236-0.9951 for PP. This trend indicates that the empirical and semi-empirical models fit the experimental data better than the theoretical models. Although the gasification reactions are best simulated by the empirical and semi-empirical models, there are no physicochemical implications that can be deduced from these empirical models. These models are modified versions of the theoretical models which includes arbitrary constants that has no physical meaning and are intended solely for the purpose of generating a best fit model. For the theoretical models, the RPM was the best model to simulate the gasification reactions. This indicates that the gasification of HDPE and PP simulate that of porous feedstock, where the gasifying agent is diffused throughout the porous structure of the feedstock, as opposed to surface reactions, which would be the case for SCM.

Using the EMVM calculations, the activation energies of the HDPE feedstock were plotted against the catalyst loadings. Upon closer observation, the activation energies obtained for 700°C and 800°C are nearly identical, with a 10 kJ/mol difference except for the experiments with 5% loading. This indicates that,

for the mid-range temperatures of 700°C and 800°C, catalytic activity is stable and the rate of gasification is not significantly affected by the increase in temperature. This may further indicate that at 5% loading of the catalyst, a saturation effect is observed in which high amounts of the catalyst will not significantly affect the rate of gasification even at elevated temperatures. Unlike the results with HDPE, however, the gasification of PP shows erratic catalytic activity, with no clear pattern or range of values observed at all set programmed temperatures. This is consistent with the observation that PP is more difficult to gasify due to the complexity of the repeating units in the polymer (Bai, Wang, & Jin, 2019). Similar to HDPE, the apparent rate constants calculated using EMVM for the gasification of PP and no noticeable trend was observed. The apparent rate constants for PP, however, were generally lower than that of HDPE. The average apparent rate constants (k) for both RPFs were calculated for each experimental run and the results are shown in **Table 3.3**.

Table 3.3 Average rate constants (k) for the gasification of HDPE and PP using EMVM

Temperature (°C)	Catalyst Loading (wt %)	Average k (min^{-1})	
		HDPE	PP
600	0	1.3867	1.6875
	1	1.3107	1.1549
	3	1.6717	0.9748
	5	1.8645	0.7721
700	0	1.9643	2.3134
	1	2.3364	1.4512
	3	2.2813	1.6288
	5	1.9232	1.5784
800	0	1.9049	1.4161
	1	1.7274	1.0021
	3	2.1953	1.3158
	5	2.0237	1.7291
900	0	0.3018	0.7973
	1	2.0746	0.8427
	3	2.3561	0.7949
	5	1.6449	1.5159

4. CONCLUSIONS

Based on the results obtained, for HDPE, the lowest activation energy was achieved at gasification temperature of 900°C. For PP, however, the lowest activation energy was observed at a temperature of 600°C and catalyst loading of 5%. In most runs, it was observed that the catalyst becomes less effective as the catalyst loading increases which is due to saturation effect. The extended modified volumetric model (EMVM) was evaluated to be the most effective in simulating the gasification reactions among the empirical models while the random pore model was effective among the theoretical models.

With the small effect of the catalyst on the rate of gasification, it is necessary to modify the sample in terms of its size, porosity and surface area. It is also necessary to use smaller catalyst loading to prevent saturation effect and the consequent decrease in the porosity of the sample due to the increase in the concentration of the catalyst.

5. REFERENCES

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