

TGA-DSC: A Screening Tool for the Evaluation of Hydrocracking Catalyst Performance

Muhammad Salman^{1*}, Shazia Nisar¹, Zahid Hussain², Hina Salman², Mohib R. Kazimi³

¹Department of Chemistry, University of Karachi, Karachi, Pakistan

²Institute of Chemistry International Center for Chemical and Biological Sciences, University of Karachi, Karachi, Pakistan

³Department of Applied Chemistry and Chemical Technology, University of Karachi, Karachi, Pakistan

Email: msqureshi98@gmail.com, zahidku@yahoo.com, mehandy15@hotmail.com, mrkazmi@uok.edu.pk

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Abstract

DSC-TGA was used for screening of commercially available and synthesized catalyst for the degradation of polypropylene (PP). In this study, all the runs were performed with 50% load of the catalyst and the results were compared with those of PP + 50% pure silica having no catalytic activity. The degradation behavior of PP using catalyst Zeolyst-713 exhibited much higher degradation activity among the other catalysts used in this study. Moreover, it contributed to lowering of initial stage temperature showing a shape-selective effect. DSC-TGA tools such as T_{on} , T_{max} , $T_{99\%}$, activation energy, enthalpy change in the process and coke content were used for screening. It was concluded that the pore construction and unique acid properties of the Zeolyst-713 as well as proper reaction temperatures were significant influential factors to fully exert this effect. In this work, kinetics of catalytic thermogravimetric degradation of PP used for domestic purposes was investigated using Alumino-silicate catalyst. Zeolyst-713 was observed to lower activation energy and enhances degradation activity in comparison with thermal degradation without a catalyst.

Keywords

Thermogravimetric Analysis (TGA), DSC, Pyrolysis, Catalytic Degradation, Polypropylene Waste Plastic, Catalysis

*Corresponding author.

1. Introduction

The quantity of plastic wastes generated by our society are on the rise. There is no option except recycling for conservation of resources and environment [1].

Being a low biodegradable material, recycling of plastic waste has become one of the front line issues these days. Moreover, large scale production poses serious environmental problems, necessitating awareness of source reduction, re-use and recycling and propose environmentally friendly solution. Polypropylene, one of the core components of waste plastic is widely used as industrial thermoplastic. However, for polyethylene-terephthalate (PET) and other linear polyesters, chemical and physical recycling to lower grade plastics is available, but, most of the plastic wastes are either incinerated or buried that consequently cause aesthetic and environmental hazards. Given that incineration could not be the best possible option and might pose serious environmental problems, for sustainable growth and environmental protection, upgrading of waste plastic is necessary.

Among available options catalytic degradation requires lower temperatures ranging from 350°C to 550°C than thermal ranging between 500°C to 900°C, with production of more valuable products [2]-[8]. In addition, several studies have been reported using known hydro-cracking catalyst widely used in oil industry.

Activities of acidic catalyst on cracking of plastics were reported by Negelein *et al.*, (sulfated zirconia, a strong acid catalyst, known to lower cracking temperature and facilitate the mechanism of hydride abstraction) [9] and Akpanudoh *et al.* [10]. Zeolite Y. and ZSM-5 accelerated the degradation of high density polyethylene (HDPE) through reducing the activation energy of the process. ZSM-5 also exhibited lower coke deposits compared to Zeolite Yas reported by Garforth *et al.* [11]. Acidity of catalyst is related to the degradation process. The higher the acidity of the catalyst, the higher is the resultant degradation with an increase in volatile saturated products. Akpanudoh *et al.*, also showed that HZSM-5 and silica-alumina catalysts mainly produce olefins as primary volatile products. It was observed that polymer degradation was more efficient in the presence of the catalyst. Similar results were observed by Araujo *et al.* [12]. PP is an easily degradable compared to low density polyethylene LDPE and HDPE [13].

Extensive work has been done for the characterization of the catalyst for plastic degradation and most commonly, TGA instrument has successfully been used. TGA-DSC analysis serves primarily as an assessment tool in the screening of various potential catalysts for polyolefin pyrolysis prior to the micro reactor or to a pilot plant.

This study screens the synthesized and commercially available catalyst performance of varying acidity, pore volume and surface area by TGA indices. PP has 25% market share in world consumption throughout the world among thermoplastics. Consequently, PP widely used in domestic and commercial application, had been selected for this study. The synthesized catalyst is a composite of USY zeolite and titania-alumina. TGA facilitates the investigation on degradation kinetics during pyrolysis of waste plastics [14]-[18]. In inert atmosphere and constant temperature ramping program it provides details of thermal events of plastic during pyrolysis by plotting weight loss of the sample as a function of temperature, crucial for designing and conversion on industrial scale. TGA method developed here for catalytic degradation would help in the development of cheaper catalyst.

2. Experimental

2.1. Polymer

The model plastic polypropylene (PP, Mn = 75,000; d = 978 kg/L) was used in this study.

2.2 Catalyst

Five catalysts were used and these were given numbers, C-1 to C-5 and C-6 which is pure silica (not a catalyst), for their identification. Catalyst C-1, being titania based, was synthesized in our laboratory according to the method described by Ali and Asaoka [19] and the procedure described elsewhere in [20]. Catalysts C-2 to C-5 were purchased from commercial sources largely used by petroleum refiners. RCD-8 is a new market catalyst of UOP for fluidized catalytic cracking of petroleum residues). Before being used in the reaction experiment, the catalysts were all treated with an air stream for 4 h at 400°C for activation.

2.3 Instrument and Condition

Thermal and catalytic cracking experiments were carried out in TA Instruments SDTQ600 simultaneous TGA-

DTA-DSC thermogravimetric analyzer. Fine powder of PP and dry catalyst mixed in 1:1 ratio, with a total load of 10 ± 0.5 mg were used. Additionally, samples were treated under nitrogen with higher purge rate of 100 ml/min in an open ceramic pan to improve the external heat transfer between the molten polymer and the outside of the catalyst particles. Nitrogen flow creates an inert atmosphere for reaction while heat transfer limitation disregards with small sample size and low heating rate. The samples were then equilibrated to 100°C before being heated to 800°C at a heating rate of $20^\circ\text{C}/\text{min}$. Air was then introduced at 550°C for the determination of coke content. G. Audisio, *et al.*, observed that the inert (SiO_2) material got mixed with PP as reference to evaluate PP degradation in the absence of catalytic action is better than PP only [21] [22].

3. Result and Discussion

Degradation of PP was performed with catalysts of varying acidity, pore structure and surface area in a refinery and compared with the synthesized catalyst. Instead of pure PP, inert material (SiO_2) similar in surface area to the catalysts was chosen as reference to evaluate PP degradation in the absence of catalytic action as shown in **Figure 1(a)** & **Figure 1(b)**. G. Audisio *et al.*, showed insignificant catalytic effect of SiO_2 on PP degradation in terms of product yields and distribution also concluded that such reference is more adequate than pure PP [21] [22].

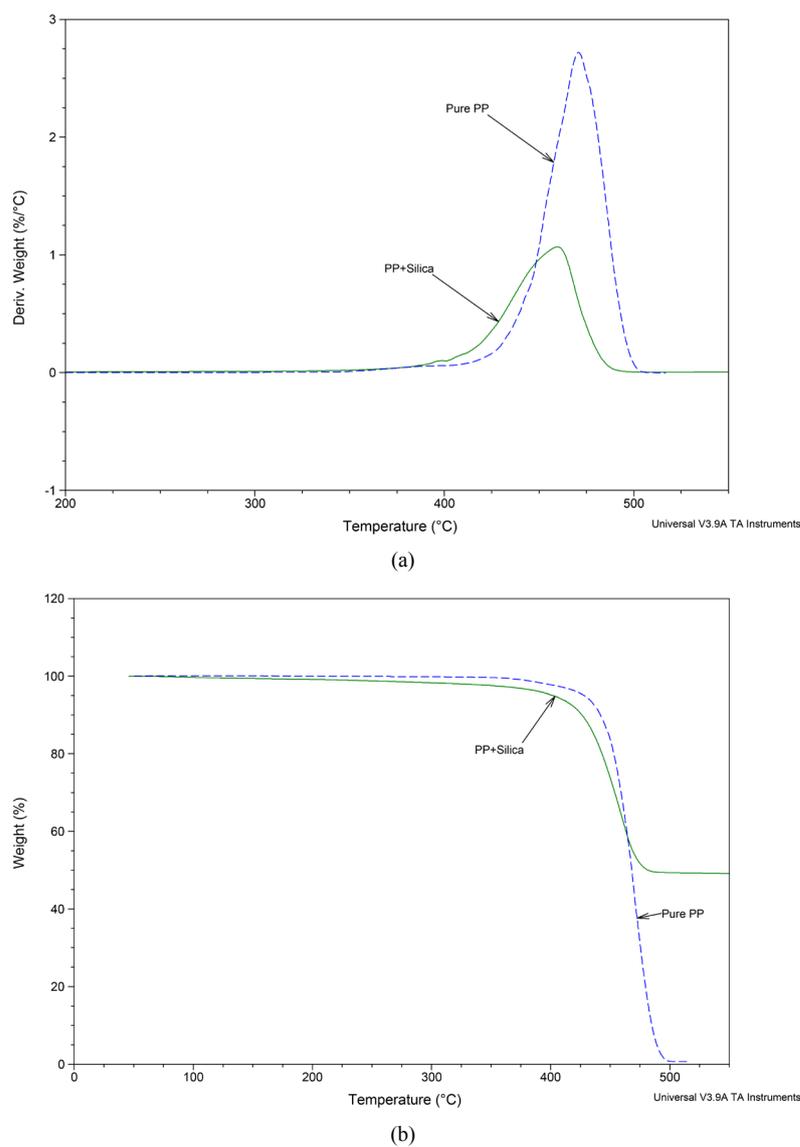


Figure 1. (a) Over lay of DTG curve of PP and PP + 50% SiO_2 ; (b) Over lay of TG curve of PP and PP + 50% SiO_2 .

The use of acid catalyst can enhance thermal degradation of synthetic polymers that could be monitored by thermogravimetry. For the present study, catalyst of wide ranging acidity and surface area was used. The detailed characteristics of the catalyst being in an amorphous form ($\text{SiO}_2\text{-Al}_2\text{O}_3$) are given in **Table 1**.

Product distribution in the results of pyrolysis depends on both the pore size and acidity of the catalyst [1].

The decomposition of polymer is very complex radical chain mechanism, involving initiation, propagation and termination reactions. Degradation of PP under different heating rates and carries gases reported in literature [23] [24] [27] [28]. Polymers are long chain macromolecules with high viscosity during degradation, it is assumed that the polymer macromolecules break down initially at the exterior of catalyst surface and then small fragments enter into the inner pore structure of catalyst to undergo further reactions [29].

The differences obtained for polymer degradation could be explained by different Si/Al ratios as well as their porous structure: higher Si/Al means a reduction in the number of Al^{3+} cations in the adjacent positions, which provides strong Brønsted acid sites due to their isolation [24] [30]. Acid-catalyzed degradation of hydrocarbons is recognized to proceed via carbonation mechanisms, initiated either by proton donation (Brønsted acid sites, strong acid sites) or by hydride abstraction (Lewis acid sites, mild acid sites) [24] [31]. In the case of HY zeolite, the initial polymer cracking most likely occurs at the acid sites positioned at the exterior surface of the zeolite crystals or at the openings of pores. This cracking produces smaller molecules, which are able to diffuse in to the interior of zeolite and transform into coke due to the strong Brønsted acid sites being there, leading to obstruction of the microporous structure [32]. PP is easily degradable compared to LDPE and HDPE [13].

Although the process of catalytic degradation of PP is far from an elementary reaction, kinetic information derived from the thermogravimetric analysis and properties such as activation energies could be obtained from TG data. Reactions conducted in the bulk polymer involve more serious problem of heat transfer and mixing efficiency than those observed for small TG samples. 1:1 ratio eliminates the bulk pyrolysis of pure PP and influence of the catalyst on PP degradation could readily be determined by carrying TG experiments that allow useful comparison. For the characterization of thermal degradation process the experimental indices onset temperature (T_{on}), temperature of maximum rate of degradation (T_{max}), energy required during main degradation step, the apparent activation energy of degradation process (E_A) and remaining coke content were used. For the minimization effects of parallel non-catalytic bulk pyrolysis, effect of heating rate, and to reduce the instrumental and mixing variation, multiple runs were performed till the difference of T_{max} for same composition became 2°C and that of enthalpy change in the process differed to 5 j/g.

In **Figure 2(a)** & **Figure 2(b)**, the mass loss (TG %) curves of all studied samples are presented at a heating rate of $20^\circ\text{C}/\text{min}$. Pure PP initiated thermal degradation at about 380°C , while the presence of catalyst caused a shift of initial mass loss towards lower temperatures depending upon the catalyst performance. There was a clear shift of initial decomposition temperature of almost all catalysts except C-5.

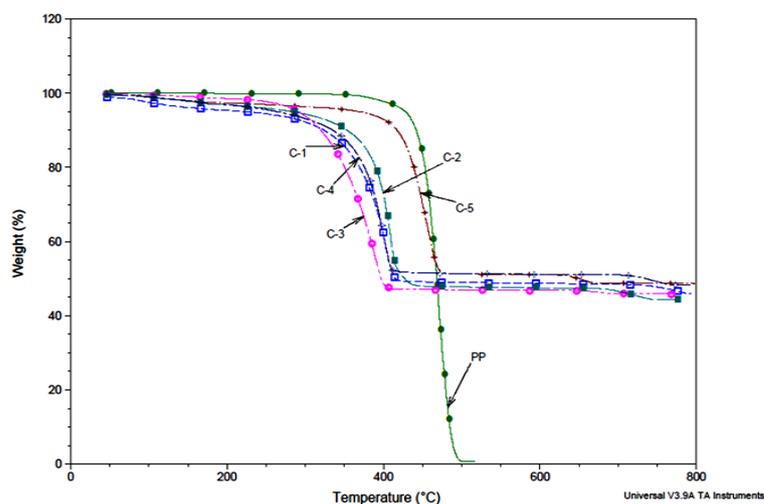
The temperatures of onset, T_{on} , $T_{99\%}$, and temperature at maximum-rate T_{max} , for the degradation were examined on the basis of the derivative thermogram and a significant decrease was found in the presence of catalysts, except for C-5, as shown in **Table 2** and **Figure 3**. Plastics with similar structure—HDPE & LDPE—had $T_{99\%}$ in the range of 491°C - 505°C [3]. T_{on} values for PP over C-3 were smaller than those of the other catalysts. These results indicate that C-3 lowers PP decomposition temperature considerably. The order of decreasing T_{on} is as below.

Table 1. Characteristic of used catalyst.

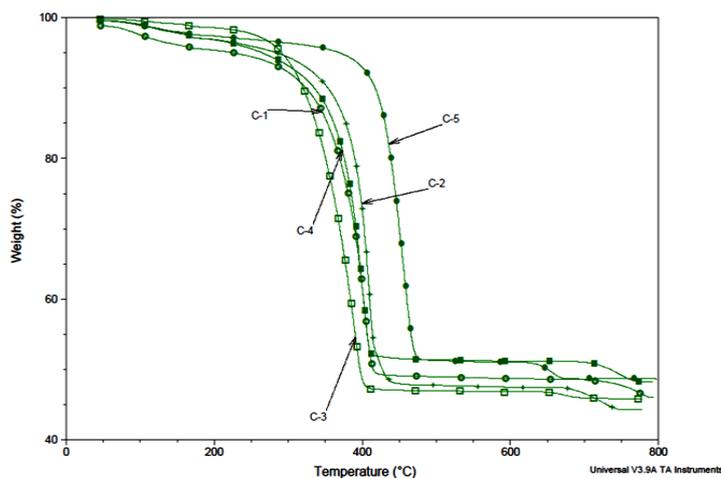
Name	Description and composition	Surface Area m^2/g	Pore volume cc/g	Total acidity	Wt.% loss at 100°C
C-1	NiMo loaded on [TiO_2 + alphaalumina + AP-1 + USY] Extrudates	359.0	0.42	1.48	4.6
C-2	KC-2710 (AKZO Nobel)	182.0	0.23	2.96	8.40
C-3	Z-713 (Zeolyst International)	221	0.34	1.41	4.57
C-4	HC-100 (UOP)	231	0.25	3.67	9.73
C-5	RCD-8 (UOP)	210	0.21	2.19	6.28
C-6	SiO_2	550	1.2	1.59	1.10

Table 2. Comparison of onset-temperatures (T_{on}), $T_{99\%}$, moisture% and maximum-rate temperatures (T_{max}) for PP degradation on catalyst and on SiO_2 (inert reference material).

Name of catalyst	T_{on} (K)	T_{max} (K)	$T_{99\%}$ (K)
C-1	386	409	421
C-2	388	421	449
C-3	351	358	403
C-4	365	405	444
C-5	432	457	476
C-6	454	475	501



(a)



(b)

Figure 2. (a) Over lay of TG curve of PP and PP + 50% SiO_2 ; (b) Overlay of TGA curve of PP + 50% Silica with 50% load of catalyst.

$$C-6 > C-5 > C-1 > C-2 > C-4 > C-3$$

The analysis of the thermograms of catalysts **Figure 4** shows a regular decrease in weight versus temperature. Such weight loss occurs with a quite constant rate. This weight loss is missing in the run of pure PP.

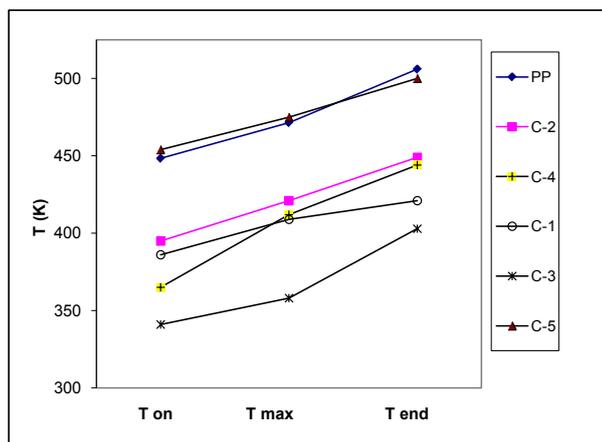


Figure 3. Comparison of T_{on} , T_{max} and T_{end} of studied catalyst.

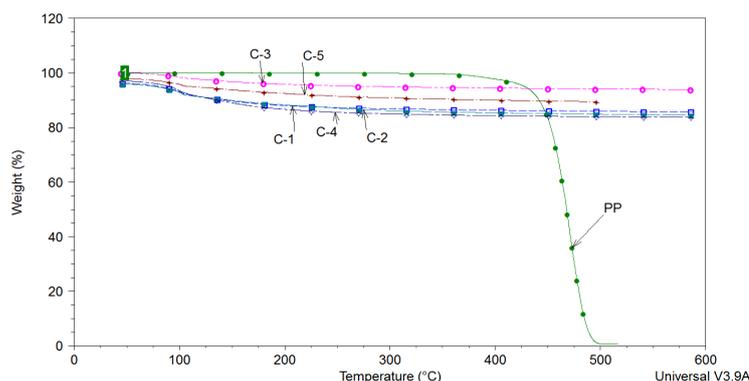


Figure 4. Overlay of TGA of used catalyst C-1 to C-5 and pure PP.

These observations were compared with the thermal analyses of each catalyst without polymer to evaluate the weight variation related to the catalyst. It is evident that a slight, but not negligible, loss of weight is attributable to the catalyst, probably due to the release of physical and structural water, occurring next to the major weight loss in PP sample. The weight loss of catalyst was relatively small and relatively linear with temperature. Weight loss is more important after 100°C at higher temperatures as summarized in **Table 1**. Moisture content depends on structure, pore volume and acidic property of the catalyst. T_{max} indices of the catalyst are in the following order.

$$(C-6 >) C-5 > C-1 > C-2 > C-4 > C-3$$

3.1. Kinetics of Polymer Degradation

Arrhenius Equation was applied for the determination of activation energy and pre-exponential factor. Activation energy (E_a) with 50% catalyst load was determined by equation 4 and is summarized in **Table 3**. From main degradation steps, 10 to 90% data was selected for kinetic evaluation. The activation energy for the pyrolysis of virgin PP with 50% SiO_2 was found to be 310.7 kJ/mole. A considerable decrease in Activation energy was observed with the catalyst, but this effect was not very significant when using C-5.

Kinetic parameters were determined on the basis of two assumptions: 1) the degradation reaction is of the first order and 2) catalytic decomposition is dominant, by integral method and Equation (1) [25] [26].

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-x) \quad (1)$$

where x could be determined by:

$$x = \frac{W_o - W_t}{W_o - W_f} \quad (2)$$

Weight loss rate was calculated by the following expression.

$$\frac{dW}{dt} = -\frac{1}{W_o} \left(\frac{dW_t}{dt} \right) \quad (3)$$

where W_f is the final mass at the end of pyrolysis (here at 99% of main degradation step), W_o is the initial weight loss and W_t is the weight loss at time t .

For a constant heating rate Equation (1) is rearranged as follows.

$$\frac{\ln(-\ln(1-x))}{T^2} = \ln \left[\frac{AR}{HE} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (4)$$

For constant heating rate $H = \frac{dT}{dt}$.

Plotting of graph between $\ln[-\ln(1-x)/T^2]$ versus $1/T$ of PP showed linear dependence on temperature as shown in **Figure 5**, slope of the curve gave the E_a value as summarized in **Table 3** [25] [26]. **Figure 5** shows the pictorial graph of PP degradation and **Figure 6** depicts E_a comparison.

Figure 6 showed that for C-5 although T_{max} , T_{on} and $T_{99\%}$ not lower considerably but they decreased activation energy compared, with without catalytic reaction. This is evidence for some catalytic activity but different product distribution that ultimately leaves residue.

On the basis of T_{max} , T_{on} , $T_{99\%}$ and activation energy values, C-3 was found to be superior over other catalysts

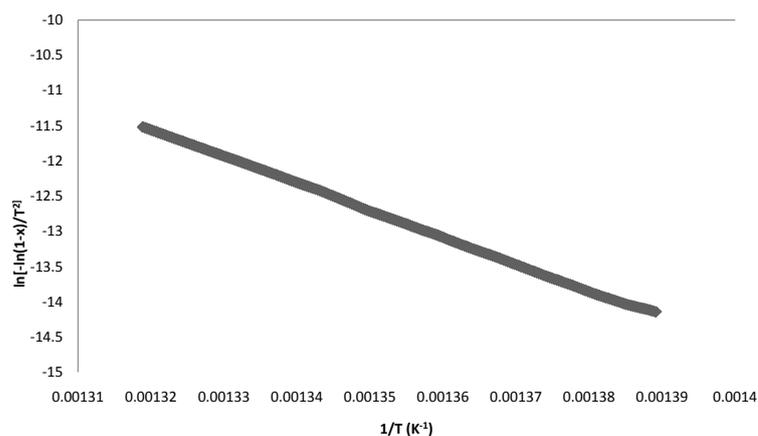


Figure 5. Graph between $\ln[-\ln(1-x)/T^2]$ versus $1/T$ for determination of E_a of pure PP.

Table 3. Summary of E_a value.

Catalyst	Catalyst ^a (% w/w)	Activation energy (E_a /kJ mol ⁻¹)	Regression for line used for E_a
C-1	50	76.94	0.967
C-2	50	80.09	0.982
C-3	50	65.26	0.973
C-4	50	72.77	0.964
C-5	50	115.3	0.955
C-6	50 (silica)	310.7	0.993

^aMeasured weight fraction.

used during this study and was selected for stepwise E_a calculation. Stepwise E_a was determined through the splitting of whole process into different steps, taking 0 to 10% as independent single step up to 90% to 100% for the main degradation process only for C-3 which is shown in **Table 4**. **Table 4** indicates that after each step, activation energy is increased showing that as degradation proceeds, heavier molecules remain in pan which ultimately depends on preceding steps and results in residue in TGA pan. In TGA run where no hydrogen is added to the system, initially lower molecular weight hydrocarbons with high H: C ratio mainly in gaseous state are formed.

3.2. Amount of Coke/Waxy Material

TGA is also a good tool for the determination of Coke content [1] TG run turns catalyst black most probably due to residual compound formed during pyrolysis, when operated up to 500°C. The formation of coke is equally probable. For the estimation of coke/residue content the reaction mixtures were heated further up to 800°C by the introduction of oxygen in the system that burn the remaining coke/residue present even in the lattice of catalyst. This weight loss is shown in **Figure 7**. Despite the weight loss due to moisture initially weight loss is the major reaction that produces the product of interest and was therefore selected for the kinetic study.

Further use of second weight loss had its utility for the determination of catalyst performance. Of course, the second weight loss is equally important for the screening of catalyst. More coke/residue product forming catalyst blocks the active catalyst sites and needs to be reactivated for reuse. The quantities of coke produced in the reaction are directly related to the specific structure of the catalyst. If the sizes of the pore are insignificant the

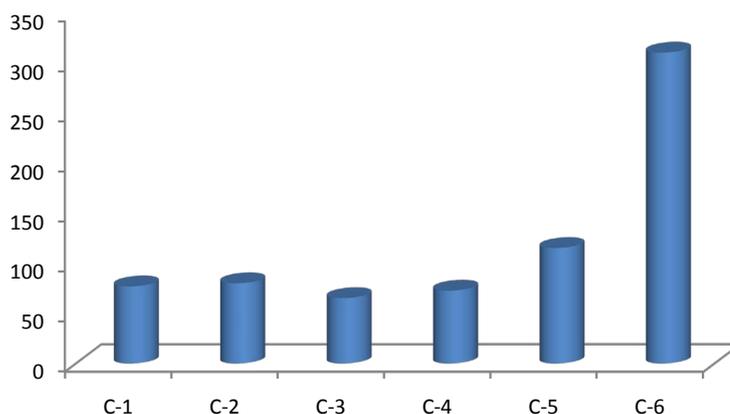


Figure 6. Comparison of activation energy for C-1 to C-6.

Table 4. Step wise E_a for C-3 in main degradation step.

% of PP	Activation energy E_a (kJ/mol)	Line regression
0 - 10	43	0.976
10 - 20	68	0.994
20 - 30	102	0.966
30 - 40	154	0.981
40 - 50	193	0.979
50 - 60	232	0.972
60 - 70	277	0.958
70 - 80	300	0.986
80 - 90	342	0.969
90 - 100	361	0.980

accumulation of large cracked molecules is not allowed. It has been reported that due to their specific relatively narrow pore size and structure ZSM-5 Zeolites have low coking properties. Small pore size does not allow deposition of bigger cracked molecules into the pores as compared to Zeolites of other type [33]. For direct application, the regeneration of catalyst is very crucial. Enormous amount of heat is generated during this exothermic process as shown in DSC curve **Figure 8**.

This generated energy perhaps might be used for activation catalyst for new feed. If the removal of coke is not fully accomplished, it may cause catalyst deactivation. Each cycle of polymer addition may introduce a limit in the use of polymer/catalyst ratios; one has to either introduce more fresh catalyst or to regenerate it. The quantity of coke/residue production is directly related to heating rate, acidity of catalyst, outer and inner acidic sides of catalyst pore size and surface area of catalyst. A logical guess suggests that pyrolysis products of high C:H ratio gives low coke content and vice versa, therefore, this weight loss has its utility for the screening tool of catalyst performance.

Table 5 summarizes the coke/residue content with each catalyst. During degradation C-3 distributes products selecting lowest energy path in such a way that only small amount of coke/residue remains in the pan and proves superiority over the other. Coke/residue content has the following decreasing order.

$$C-2 > C-1 > C-4 > C-5 > C-3 (> C-6 \text{ pure silica})$$

3.3. DSC Study

Catalysts not only lower the activation energy and T_{\max} but also lower the required energy in main endothermic

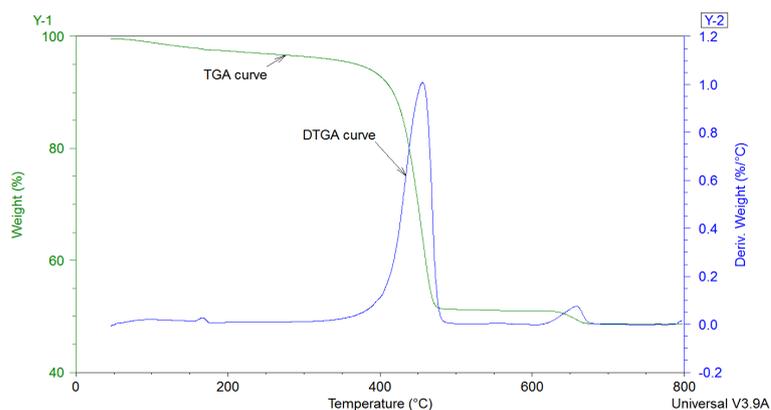


Figure 7. DTGA & TG curve of PP with 50% catalyst.

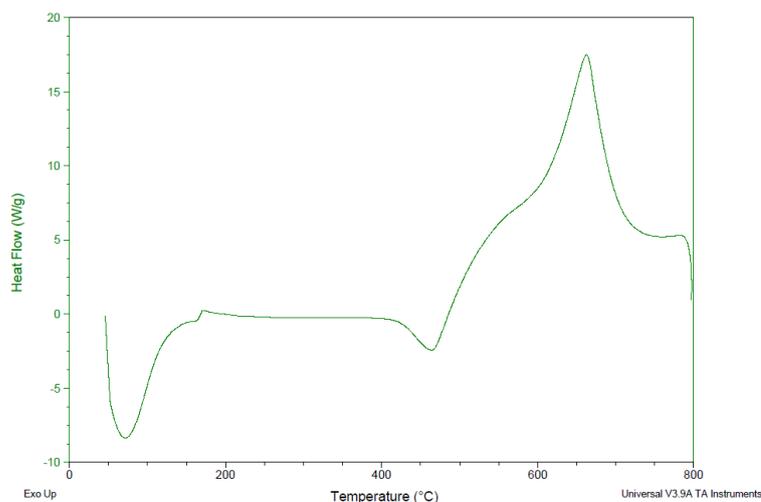


Figure 8. DSC endothermic and exothermic profile of PP with 50% catalyst.

process. **Figure 9** shows not only a shift of T_{\max} but a curve depicts endothermic behavior. Activation energy has its own utility but in closed continuous reaction vessel, once the feed is activated, the extra amount of energy is used to activate new feed and the energy required for the process becomes very important as it actually determine the cost of the process. Energy required for the process is also important parameter for catalyst screening.

The catalyst degrades plastic in such a way that in each step molecules requires lower enthalpy of reaction and it depending upon the catalyst's acidic active site and pore structure, ultimately its performance is determined. **Table 5** shows the energy required for each used catalyst and are compared with PP with 50% SiO_2 . It is observed that the catalyst lowers the required energy than thermal degradation. Only C-3 was found to be considerably superior, whereas C-5 didnot lower the energy significantly. TGA facilitated determination of enthalpy change during the reaction which provide ultimately helpful for the screening of catalyst for its activity for degradation. Linear curve was used for estimation of enthalpy change in the process.

4. Conclusions

The values of T_{on} and T_{max} are correlated with the kinetics and the mechanism of the degradation. The two measures, T_{max} as well as T_{on} can be regarded as good direct measures of the catalytic effect. In the present study it is apparent that the influence of the catalyst on PP degradation could be examined on the basis of kinetic parameters derived from kinetic interpretation from TG data.

For the pilot plant and direct application, the regeneration of catalyst or the removal of high molecular compounds is very crucial. The energy released on the burning of formed products that is an exothermic process produces the enormous amount of heat depending upon the amount of products. This generated energy might be used for the activation of fresh added feed of polymer in the plant. Catalysts that provide lowest energy path for degradation are of superior activity than others. They are economical and hence save energy and money. Moreover, they are also easy to handle.

Catalytic activity for degradation and product distribution are shared effects of acidity surface area and pore

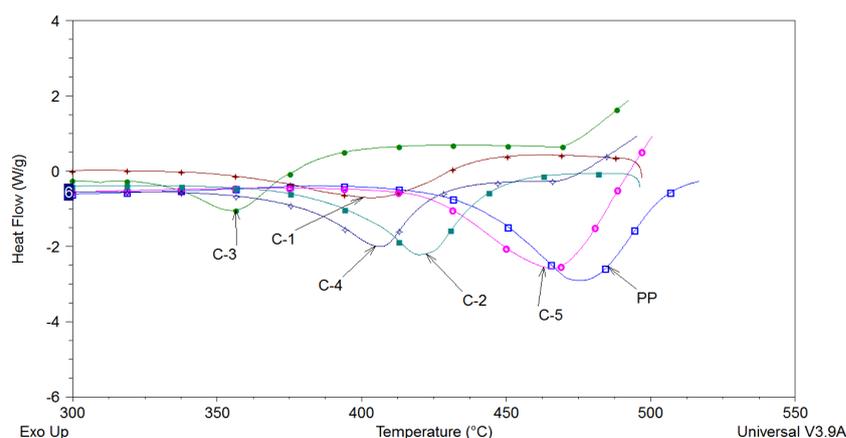


Figure 9. DSC endothermic curve of PP with all studied catalyst at 50% load.

Table 5. Coke/residue content and energy used in the endothermic curve.

Catalyst	Catalyst ^a (% w/w)	Coke content (%w/w)	Heat use (j/g)
C-1	50	2.073	215
C-2	50	3.356	219
C-3	50	1.005	173
C-4	50	2.889	186
C-5	50	2.424	230
C-6	50 (silica)	0	228

^aMeasured weight fraction.

volume. Coke content, energy consumption, enthalpy change, activation energy and T_{\max} are good indices for catalyst performance evaluation. In this study, Zeolyst Z-713 was found to be superior over other used catalysts that lower coke content, activation energy, T_{\max} and enthalpy required for the process.

In this work a novel usage of TGA, is done in terms of screening of catalyst. The procedure not only proved to be time-saving and cost effective, but also highly accurate. An overall result demonstrates an ideal stage for implementation at pilot plant level. Important parameters of TGA run will be used to calculate T_{on} , T_{\max} , $T_{99\%}$ coke content and enthalpy for monitoring hydro-cracking catalyst performance.

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