

# **Fuel from Waste - Catalytic degradation of plastic waste to liquid fuels**

## **Extended abstract**

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### **1. Introduction**

In this work, thermal and catalytic degradation of polypropylene with, and without additives are analyzed using thermogravimetry (TG) and differential scanning calorimetry (DSC) methods under a nitrogen atmosphere.

During first part of the experiments the thermal pyrolysis of both types of polypropylene was carried out using non-isothermal conditions, with different heating rates.

In the second part of the experiments the catalytic pyrolysis of the same polypropylenes was analyzed using 3 groups of catalysts:

- zeolites, namely HZSM-5, HY, Beta and H-Beta
- vermiculites with supported metals, namely silver, zirconium, alumina and copper,
- montmorillonites, including  $Mt_6OAlCu$ ,  $K10 + Cu^{2+}$  and  $K10 + Al Ag^+$ .

From the results obtained, the zeolites were the most effective catalyst for the reduction of the temperature of degradation. Montmorillonites were also somewhat effective for the polyolefin pyrolysis.

In contrast, vermiculites, particularly those with metal supported, showed an apparent inactivity proving to be ineffective in the reduction of the temperature degradation.

The simultaneous use of the signals from the TG and DSC helped to develop a kinetic model that is able to describe runs performed for the thermal degradation of both types of polypropylene. Fitting this model to the experimental results allowed the estimation of several kinetic and thermodynamics parameters associated with the degradation of polypropylene.

There are many technologies and reactors than can be used to pursue the reaction, but due to the nature of the pyrolysis, thermogravimetric analysis (TGA) is widely considered as a useful technique to study the degradation processes and its kinetics.

However, with TGA the reaction is only detected after it has occurred, when the products are becoming small enough to evaporate into the gas phase leading to the decrease of observed polymer mass. Taking it into account the kinetic models used to described the process are basically based on the weight loss analysis curves obtained during thermal gravimetric analysis of the polymeric samples. A similar objection can be raised when only the gas-phase products are analyzed. Anyhow, it is possible to follow the reaction from the start, since each bond of polymer that is broken consumes some amount of energy. By measuring the heat flow into the sample during the reaction (for example using DSC), it is possible to measure the rate of breaking bonds even if this leads to species that are still too heavy to evaporate and do not produce any significant mass losses and, thus, cannot be seen in the TG signal.

## 2. Experiments

The materials used in this work were both polypropylene with and without additives, kindly supplied by Borealis. Polypropylene with additives in powder form had, according to the supplier, molecular weight  $M_w \sim 290\,000$  ( $\alpha = M_w/M_n \sim 20$ ); and show melt flow indexes  $MFI_5 = 0.39/10\text{min}$ ;  $MFI_{21} = 11.8\text{g}/10\text{min}$ ;  $MFI_{21}/MFI_5 = 30$  while the polypropylene without additives samples were in form of pellets and show a molecular weight,  $M_w \sim 376\,000$  ( $M_w/M_n \sim 23$ ).

Catalyst used were respectively : *Zeolites* - HZSM – 5, HY, BEA, H-BEA ; *Vermiculites* with transition metals as catalysts, namely zirconium, alumina, copper and silver; *Montmorillonites* :  $Mt_6OAlCu$ ,  $K10 + Cu^{2+}$ ,  $K10 Al Ag^+$ .

All of the TG/DSC experiments were carried-out in a TA Instruments SDT 2960 simultaneous DSC-TGA apparatus. Before the runs, nitrogen flow was maintained through the system for 30 min to purge all the air from it. This flow rate was maintained during the experiments.

The PP samples, pure or along with the catalysts were placed in quartz TG pan and the thermal degradation was analyzed. The PP/catalyst mixture was prepared at room temperature in order to obtain 15-25 mg of mixture. The quantity of catalyst used was approximately 1-3mg, depending on the experiment.

The first part of the experiments was carried out using dynamic conditions, by raising the temperature with different heating rates. The runs were performed under nitrogen with continuous flow rate 80ml/min, with various heating rates: 10,20 and 40 °C/min. The temperature was going up from room temperature up to 600 °C. This temperature was maintained for an additional 10 min. Experiments with various heating rates were performed for non-catalytic degradation and for degradation with H-ZSM catalyst. For the rest of experiments with catalyst the heating rate was equal 10°C/min.

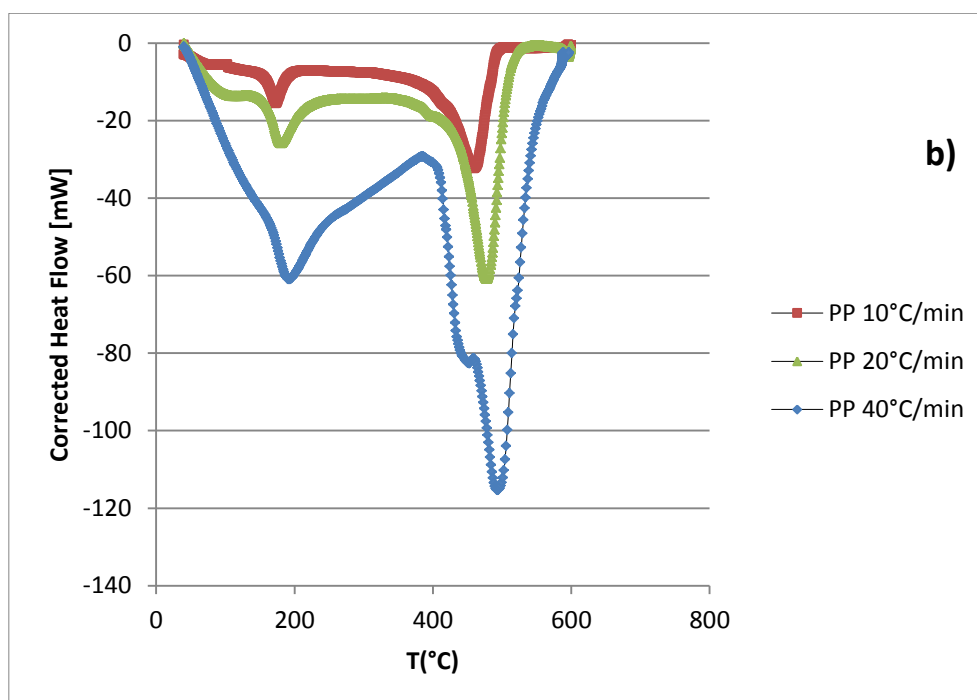
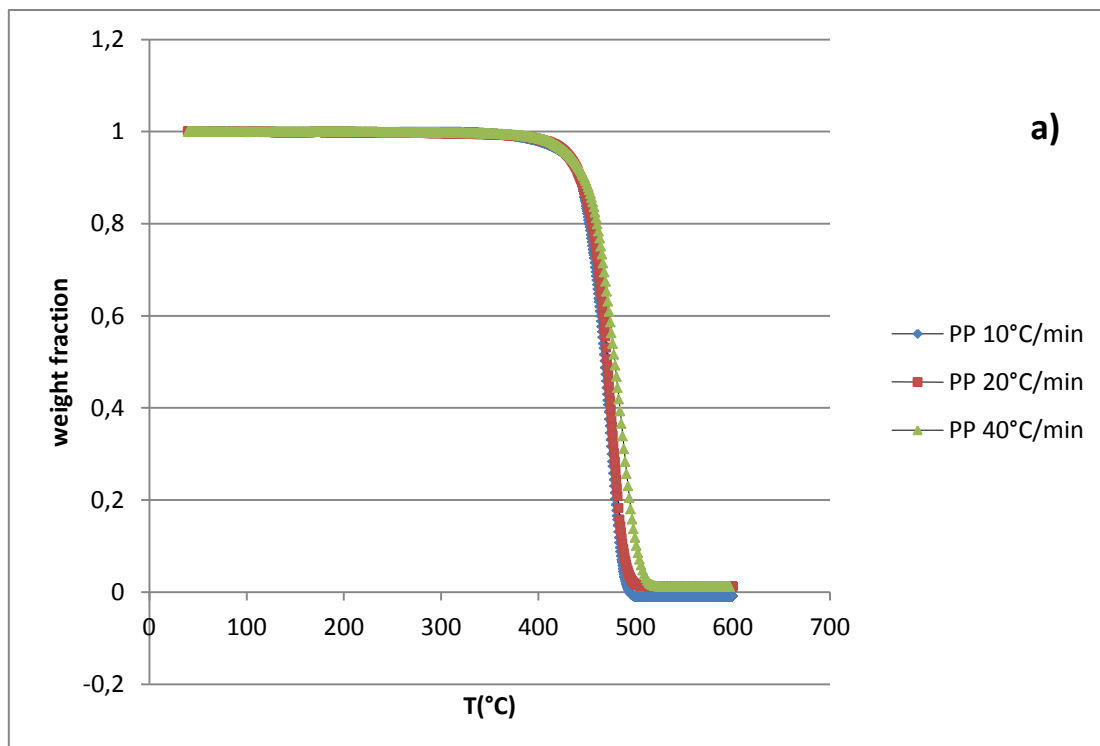
### 3. Thermal degradation of polypropylene

The results obtained from the DSC/TG analysis on PP with additives sample for four different heating rates are shown in figure 1.1. Picture (Figure 1.1b) shows the curve corresponding to the DSC signal with two endothermic peaks. The first one corresponds to the melting of the polypropylene sample, which occurs at 136 °C/min and has no significant weight change, as it can be seen in Figure 1.1a. The second endothermic peak occurs at higher temperatures and is related with polymer degradation. This peak is accompanied by a weight loss. The start of the second DSC signal is due to the energy which is given to the sample when the bonds in the polymer begins to break. This breakage of the bonds in the polypropylene produces increasingly lighter products that will become sufficiently small to be volatile at the temperature of reaction and will evaporate from the pan, leading to the easily observed mass losses as well as to additional consumption of energy.

The temperature at which polypropylene with additives suffers thermal degradation when using heating rates between 5 and 40° C/min are in the range of 458 to 488°C . The list with all temperatures at which the maximum rate of heat consumption occurs for this process are presented in table 1.1 for the different heating rates.

**Table 1.1-** Degradation temperature for the polypropylene samples obtained from TGA/DSC results.

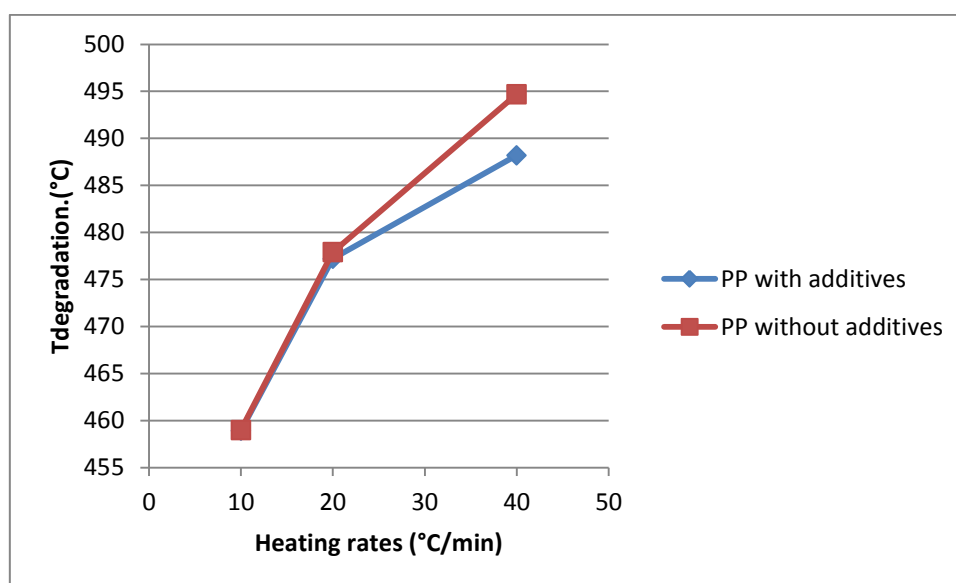
| Sample                | T <sub>degrad.</sub> (°C) |
|-----------------------|---------------------------|
| PP with add. 10°C/min | 458,9                     |
| PP with add. 20°C/min | 477,2                     |
| PP with add. 40°C/min | 488,2                     |



**Figure 1.1** – TG (a) and Heat Flow (b) curves obtained from the degradation of PP with additives at different heating rates ( see chapter 2 for additional conditions).

## Effect on polypropylene type

The degradation temperatures for heating rates: 10, 20 and 40 °C/min are presented in figure 3.5 for the both types of polypropylene. The graph shows the dependence of the temperature at which the maximum of heat consumption occurs at different heating rates. The temperatures of degradation for polypropylene with and without additives at heating rates 10 and 20 °C/min do not differ a lot. There is a small difference between the temperature of degradation for the process at 40 °C/min heating rate – degradation of polypropylene with additives occurs at slightly lower temperature, indicating that the additives might play some role in the polymer degradation



**Figure 1.2** – Decomposition temperature dependence on the heating rates for PP with and without additives.

## 4. Catalytic degradation of polypropylene

### Vermiculites

In the table 1.2 temperatures of degradation are presented for all the experiments done with Vermiculites, as well with the temperatures for non-catalytic, thermal degradation of polypropylene

with and without additives. In both cases, presence of catalyst lowered the temperature of degradation for approximately 2-4 °C, which is not important from the economical point of view.

**Table 1.2-** Degradation temperature for PP with additives (a) and without additives (b) with catalysts Ver Zr,Ag<sup>+</sup>; Ver Al,Ag<sup>+</sup>; Ver Al,Cu<sup>2+</sup>; Ver Zr,Cu<sup>2+</sup>; VH Ag<sup>+</sup> and VH Cu<sup>2+</sup> obtained from TGA/DSC results. Heating rate: 10°C/min.

| Sample                                | T <sub>degrad.</sub> ( °C) |
|---------------------------------------|----------------------------|
| PP with additives                     | 458,90                     |
| PP with add.+ Ver Zr,Ag <sup>+</sup>  | 453,76                     |
| PP with add.+ Ver Al,Ag <sup>+</sup>  | 455,87                     |
| PP with add.+ Ver Al,Cu <sup>2+</sup> | 454,78                     |
| PP with add.+ Ver Zr,Cu <sup>2+</sup> | 455,08                     |
| PP with add.+ VH Ag <sup>+</sup>      | 455,85                     |
| PP with add.+ VH Cu <sup>2+</sup>     | 459,09                     |

| Sample                                   | T <sub>degrad.</sub> ( °C) |
|--|----------------------------|
| PP without additives                     | 459,00                     |
| PP without add.+ Ver Zr,Ag <sup>+</sup>  | 456,33                     |
| PP without add.+ Ver Al,Ag <sup>+</sup>  | 456,95                     |
| PP without add.+ Ver Al,Cu <sup>2+</sup> | 456,09                     |
| PP without add.+ Ver Zr,Cu <sup>2+</sup> | 455,08                     |
| PP with add.+ VH Ag <sup>+</sup>         | 456,30                     |
| PP with add.+ VH Cu <sup>2+</sup>        | 458,04                     |

## Zeolites

When we compare the different zeolites among each other, it can be seen (table 4.2) that the most effective catalyst for polymer degradation is HZSM-5. ZSM-5 has a high silicon to alumina ratio; the catalyst used in this set of experiments has ratio Si/Al=32 (see chapter 2). With proton (H<sup>+</sup>) as the cation, the material becomes very acidic. Thus the acidity is proportional to the Al content. For both types of polypropylenes, the lowering of degradation temperature with the presence of HZSM-5 was approximately 50 °C.

The second best catalyst from the zeolites family was HY. The main properties of this catalyst are its high concentration of active acid sites, high thermal stability and high shape selectivity. With the Si/Al ratio equal 23 it can be predicted that HY is a good zeolite for the cracking reactions.

Comparable with the HZSM-5, presence of HY also lowered the temperature of degradation for approximately 50 °C. This is observed for both types of polypropylene, with and without additives.

The presence of H-Bea catalyst lowered the temperature of degradation from 458 °C (thermal degradation) to 427 °C (polypropylene with additives) and 405 °C (polypropylene without additives). In this case there is a significant difference between lowering the degradation temperature with both types of polypropylenes. This catalyst is reported to have Brønsted acid sites in the micropores and on the external surface, and Lewis acid sites predominantly at the internal surface.

The last analysed catalyst from the zeolites, is the Bea type. In the table 4.2 it can be observed, that its presence during the degradation process of polypropylene with additives lowers the temperature degradation approximately 25 °C, and for the experiment with polypropylene without additives approximately 35 °C. It can be concluded that both zeolites, Bea and H-Bea have better influence for the degradation of polypropylene without additives (see table 4.2). As mentioned in chapter 1, zeolites are known for strong acidity and high specific surface area, but those characteristics are not enough for being excellent cracking catalysts. It was also suggested that initial polyolefin cracking occurs mainly at the acid sites on the external surface of a zeolite. Only small enough intermediates are able to enter the zeolite pores or channels and react with the internal acid sites of the zeolite. The external surface area plays more important role than the internal one for cracking of large molecules like polyolefin plastics to valuable small hydrocarbon molecules. Zeolite Bea has Si/Al ratio equal 150, which can be too high for this kind of process.

**Table 4.2-** Degradation temperature for PP with additives (a) and without additives (b) with catalysts: HZSM-5, HY, H-Bea, AISiBea obtained from TGA/DSC results. Heating rate: 10°C/min.

| Sample               | T <sub>degrad.</sub> ( °C) |
|----------------------|----------------------------|
| PP with additives    | 458,90                     |
| PP with add.+ HZSM-5 | 404,113                    |
| PP with add.+ HY     | 410,638                    |
| PP with add.+ H-Bea  | 427,034                    |
| PP with add.+ Bea    | 433,92                     |

| Sample               | T <sub>degrad.</sub> ( °C) |
|----------------------|----------------------------|
| PP without additives | 459,00                     |
| PP with add.+ HZSM-5 | 400,912                    |
| PP with add.+ HY     | 408,30                     |
| PP with add.+ H-Bea  | 405,11                     |
| PP with add.+ Bea    | 422,04                     |

## Montmorillonites

In this subsection, results from the experiments with montmorillonites are shown. From this group of catalysts 3 representative samples were studied:  $Mt_6OAlCu$ ,  $K10 Al Ag^+$ ,  $K10 Cu^{2+}$ . The same methodology, discussed in the previous sections, was applied.

A very good catalytic effect was observed from the set of experiments with  $Mt_6OAlCu$ . As can be observed in table 1.3, this catalyst lowered the temperature of degradation from 458 °C to 412 °C (polypropylene with additives), and from 459 °C to 433 °C (polypropylene without additives).

The catalysts from the K10 montmorillonite series,  $K10 Al Ag^+$  and  $K10 Cu^{2+}$ , also reduce the temperature of the degradation relatively to the non-catalytic process, although this reduction is a minor one, only about 10 – 20 °C.

All of the catalyst from the montmorillonite group were previously acidity – activated, what changed some properties of them. As mentioned in chapter 1, this activation extends the external surface area and alters the pore size distribution, which has a significant meaning for the cracking of hydrocarbons.

**Table 1.3-** Degradation temperature for PP with additives (a) and without additives (b) with catalysts:  $Mt_6OAlCu$ ,  $K10 Al Ag^+$ ,  $K10 Cu^{2+}$ , obtained from TGA/DSC results. Heating rate: 10°C/min.

| Sample                      | $T_{degrad.}$ ( °C) |
|-----------------------------|---------------------|
| PP with additives           | 458,90              |
| PP with add.+ $Mt_6OAlCu$   | 421,17              |
| PP with add.+ $K10 Al Ag^+$ | 447,22              |
| PP with add.+ $K10 Cu^{2+}$ | 422,19              |

| Sample                         | $T_{degrad.}$ ( °C) |
|--------------------------------|---------------------|
| PP without additives           | 459,00              |
| PP with add.+ $Mt_6OAlCu^{2+}$ | 433,18              |
| PP with add.+ $K10 Al Ag^+$    | 440,39              |
| PP with add.+ $K10 Cu^{2+}$    | 447,17              |



## 5. Conclusions

The pyrolytic behavior of PP with and without additives samples has been studied using TGA/DSC apparatus, for thermal and catalytic degradation.

The conclusions drawn from this work are as follows:

The simultaneous use of DSC/TG analysis provided a clear picture of the thermal and catalytic degradation processes, allowing to have a look at the reaction that occurs within the polymer before gas-phase products start to evolve. This method provided additional information enabling better understanding of the plastic decomposition mechanism.

- Comparison between the thermal degradation of PP with and without additives ( Dependence on type of polypropylene)

Degradation temperature:

The degradation temperature of the pyrolysis process is dependent mostly on the heating rates. As observed, when heating rate increase, the maximum of the heat flow curves shift towards higher temperatures. Possible explanation is due to the kinetics of the process itself and to dynamic effects of the used equipment. This behavior occurs to both types of polypropylene..

- Comparison between the catalytic and thermal degradation

Degradation temperature:

The catalytic pyrolysis of polypropylene with and without additives was also investigated using DSC/TGA analysis. For this study, although various catalysts were tested, zeolite catalysts were the most active catalysts on the reduction of the degradation temperature, with the best results for HZSM-5 and HY. Very good results were obtained for the  $Mt_6OAlCu$  from montmorillonites group. In contrast, vermiculites, both with transition metals and acidic activated, showed an apparent inactivity proving to be ineffective in the reduction of temperature process.

## Future Trends

This work was a first approach to the study of thermal and catalytic degradation of polypropylene with and without additives.

Its development allowed to arrive at some important conclusions and opened perspectives for an additional research, with the goal of getting a better insight into the process. Likewise, some aspects of the pyrolysis that was not yet clarified, can be understand now more deeply.

In future work it may be interesting to extend the study to analyze waste polypropylene, as well as other types of polyolefins.

In case of catalyst degradation, although the zeolites turned out to be the best catalyst for pyrolysis, there are a lot of studies for its influence on plastics degradation. More promising will be testing catalysts belonging to the montmorillonites, for comparative and more detailed analysis of the influence in the catalytic degradation of polyolefins. Consequently, a better characterization of the catalysts will be needed, namely in terms of surface area, acidity, pore structures and composition.

To develop a sustainable pyrolysis process, it will be required to have a detailed knowledge of the dependence between cracking conditions and product distributions.

Furthermore, evolution of the detailed kinetic measurements and computational models to explain the time-course evolution of the reaction as well as product distribution. Therefore, more detailed qualitative and quantitative characteristics of the products composition obtained in the degradation reaction is necessary.