SMARTCATs STSM- Final report

Detailed kinetic modeling of fast pyrolysis of plastics

1. Details of STSM

Applicant details

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2. Objective of the STSM

The aim of the Short Term Scientific Mission (STSM) is to extend the collaboration between the Laboratorium voor Chemische Technologie (LCT), Universiteit Gent and Dipartimento Di Chimica, Materiali e Ingeneria Chimica "Giulio Natta", Politecnico di Milano within the SMARTCATS COST action (CM1401). Plastics have become an integral part of day-to-day living, in the present century. At the same time, enormous amounts of plastics end up as wastes at both industrial and consumer levels [1]. Although traditional landfills offer easy means for its disposal, they are economically inefficient. Thermochemical recycling methods such as pyrolysis have a potential to exploit their use for the production of fuels and valuable chemicals [1-3]. A good understanding of the underlying chemical kinetics can help designing a more efficient process [4-7]. The hosting group, the Chemical Reaction Engineering and Chemical Kinetics (CRECK) headed by Prof. Eliseo Ranzi and Prof. Tiziano Faravelli, is most famous for their experience in developing detailed kinetic mechanisms for combustion, oxidation and pyrolysis of complex fuels, biomass and plastics[8]. The group has in the past developed lumped kinetic mechanisms for the pyrolysis of plastic polymers such as polyethylene (PE), polystyrene (PS), etc. [4-7]. The purpose of this collaboration was to gain knowledge on the modeling principles involved in developing detailed kinetic mechanisms of plastic polymers. The learnings from Politecnico di Milano will be in-line with the plastic waste pyrolysis experiments planned to be performed in LCT, in the coming months.

3. Work done during the STSM

Firstly, a thorough understanding was made on the methodology applied to develop the codes for the pyrolysis of plastics such as polyethylene, polypropylene and polystyrene [5-7, 9]. Later, the previously obtained data from the preliminary pyrolysis experiments of polyethylene was compared to the data published by Faravelli et al. [9]. This was done in order to estimate the differences in the product composition predicted by the code and the data obtained experimentally. As can be seen from the Figure 1 there are significant differences in the profiles of higher alkenes mole fractions. According to the theory, the formation of higher alkenes during the pyrolysis ceases after a specific molecular weight. This release of heavy hydrocarbons is determined based on the boiling point of the molecule and the pyrolysis temperature. On contrary, the mole fractions of higher alkenes was found to increase, experimentally. An extensive literature study was done to verify this observation. One argument could be that these molecules are present in the gas-phase with very small vapor pressures (not as pyrolysis products) and are detected by the GC. A few studies on HDPE pyrolysis were reported where a higher percentage of waxy/ heavy hydrocarbons were formed at lower pyrolysis temperatures. These observations, however, should be confirmed with more experiments at varying pyrolysis temperatures (low to high) to capture reliable kinetic data.
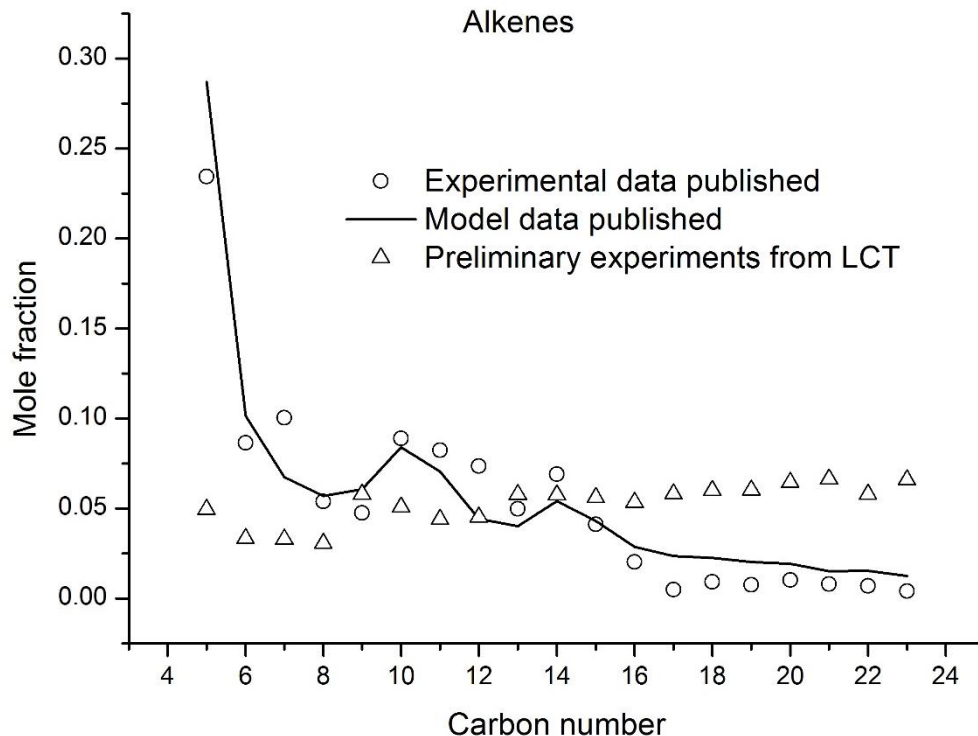

Figure 1 Comparison of LCT experimental data with that of the data published by the Faravelli et al. [9]

Further, the plastic pyrolysis codes developed in Fortran environment were revived. Each module of the code was studied to gather knowledge about its functioning. The codes were tested for their performance and fine-tuned to match the previously published data (Figure 2).

As seen in the Figure 2, the TG curves are very well reproducible. However, the product composition does not seem to match as it should (Figure 3).
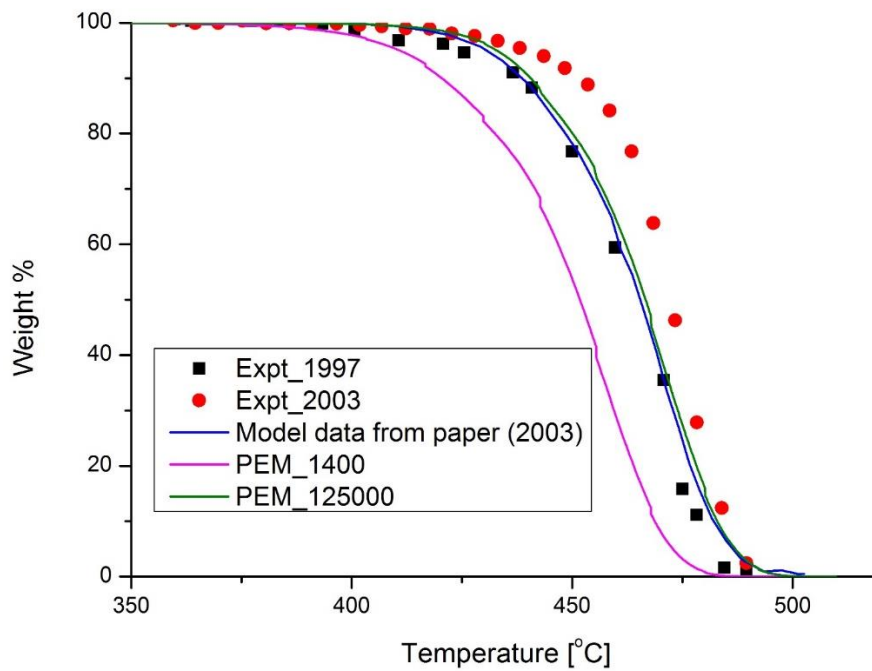

Figure 2 Fine-tuning of the model to match the published data by Faravelli et al.[5]
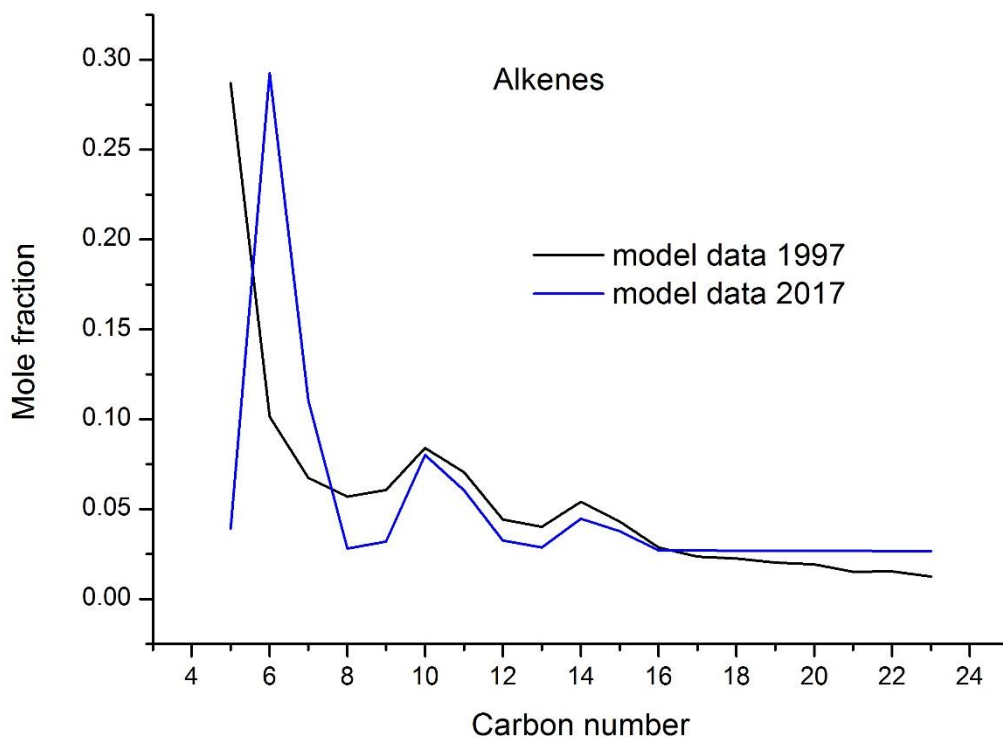

Figure 3 Product composition of alkenes as reported by Faravelli et al. [9] and those obtained by the simulations performed during STSM

On further examination of the code, it was observed that the option for gas bubble formation was disabled. From, Faravelli et al. [9] it can be understood that the gas bubble formation is very important in understanding the product distribution of gas bubbles. The products seen in the gas phase are also dependent on their corresponding diffusivities. The diffusivity of each of these products is calculated using free-volume theory [9]. In general, longer the hydrocarbon chain the lesser is its diffusivity. Thereby, the distribution of heavy hydrocarbon is low. The STSM ended with an attempt to include the gas bubble formation in the molten polymer, to obtain a product distribution in gas-phase. As shown in the Figure 4, the initial number of bubble nucleation sites had an effect on the simulated polymer decomposition. However, a few technical issues were encountered with the code before the simulations could be performed successfully.
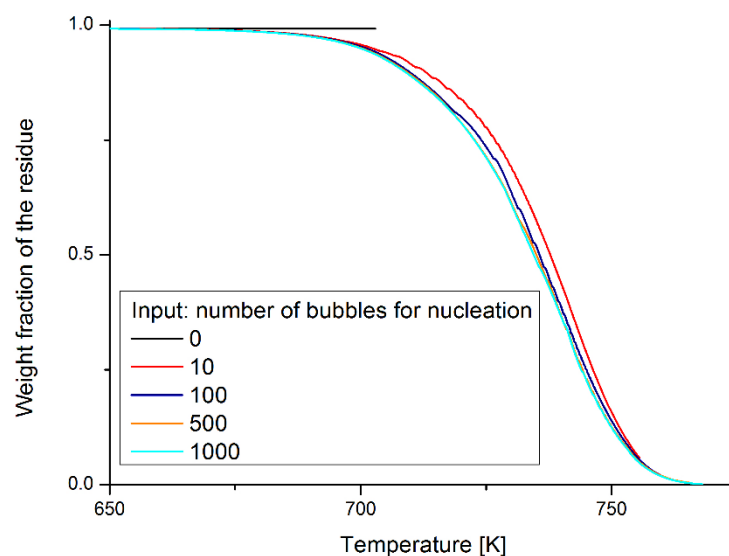

Figure 4 Effect of initial number of bubbling nucleation on the simulated polyethylene decomposition

4. Ongoing and Future work

The codes for polyethylene pyrolysis are being debugged to produce expected product distributions. Experiments on polyethylene (both HDPE and LDPE) pyrolysis will be performed to determine the effects of temperature and residence time on the distribution of gaseous and waxy products. This will also help in evaluating the performance of the currently available modeling methodology. If needed, in future, the models will be upgraded to predict more waxy products by including factors such as vapour pressure. This will be done in collaboration with the host group.

5. References

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