



THERMOCHEMICAL AND KINETIC ASPECTS OF REACTIONS RELEVANT IN WASTE GASIFICATION PROCESSES

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KEYWORDS

Pyrolysis, thermal degradation, PVC containing waste.

INTRODUCTION

The scarcity of the petroleum resources constitutes the driving force for the development of innovative methodologies for the environmentally sustainable production of fuels and energy. To solve this problem, it becomes necessary to harness the potential energy of wastes, whether industrial or municipal, through the use of valorization techniques, for the production of both energy and alternative fuels.

Despite the incineration is the most applied technique when it comes to energy valorization, two more techniques, pyrolysis and gasification, can be used presenting some advantages when compared to the previous one.

Pyrolysis is a process of irreversible chemical modification of compounds under the action of heat and in the absence of oxygen, an energy valorization technique, which causes thermal degradation. In the pyrolysis process, the reaction is endothermic and therefore requiring an external source of heat for the reaction to be initiated, always on an indirect way, neither oxygen nor water vapor are ever injected on the reactor.

The presence of organic compounds on wastes, especially plastics, is considered an important source of energy. However, most of these plastics contain polyvinyl chloride (PVC). The presence of PVC in wastes causes recycling problems when it is considered a thermal valorization process for its treatment (Borgianni *et al.* 2002), preventing the use of those residues on these processes, which main goal is the energy recovery (Kamo *et al.*; Zevenhoven *et al.* 2002).

On wastes treatments through thermal processes, such as pyrolysis, the presence of PVC in wastes containing high levels of chlorine, promotes serial pollution problems, mainly due to the formation of hydrochloric acid, chlorine gas and dioxins (Borgianni *et al.* 2002). For this type of wastes, the management hierarchy usually considered is the safe disposal on landfill, constituting a serious environmental issue (Kim 2001; Ma *et al.* 2002).

On these context, pyrolysis is considered by several authors (Zevenhoven *et al.* 2002; Kim

2001; Ma *et al.* 2002; Jaksland *et al.* 2000; Qiao *et al.*; Qing-lei *et al.* 2007; Saeed *et al.* 2004), as the most promising technique for the energy recovery from wastes containing PVC, through the thermal degradation of the chlorine molecule. Thus, it is possible to break down this molecule, allowing the chlorine recovery as hydrochloric acid or chloride (Tanaka *et al.*), with potential economic gains.

Considering thermogravimetric analysis, it is assumed that the degradation of PVC occurs between 200 and 400 °C (Zevenhoven *et al.* 2002). At 250 °C, the decomposition of PVC has already begun, with maximum at approximately 300 °C. At 350 °C the amount of chlorine present in PVC waste is already less than 0.1%, thus the PVC at 350 °C has already released 99.5% of chlorine in it (Zevenhoven *et al.* 2002). After the process of chlorine removal, there is still some residual chlorine on the waste (Tanaka *et al.*).

The C-Cl bonds in the structure of PVC have a relatively lower binding energy than the C-C and C-H bonds. This justifies the fact that the bonds of chlorine are the first to be broken, thus starting the thermal degradation of PVC (Ma *et al.* 2002; Qing-lei *et al.* 2007).

EXPERIMENTAL WORK

In this work, the kinetics of thermal dechlorination has been studied, by simultaneous DTA/TGA determinations, under inert atmosphere. The DTA/TGA experiments have been performed in a 2960 TA Instruments equipment, under controlled atmosphere obtained by a constant flow of helium over the sample.

Experiments have been done up to 5 different temperatures: 250, 275, 300, 325, and 400 °C, with heating rate of 10 °C till the desired temperature. After reaching this temperature, a stage has been done during a few hours.

The sample used to this test, was a pure PVC powder with the chemical formula C_2H_3Cl , in which 56,7 % was chlorine.

With the data from the weighing of PVC sample, in function of time, rate of change has been determined. As temperature was continuously recorded a set of values (temperature; rate of weight change) has been obtained.

Assuming the Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad \text{or} \quad \ln(k) = \ln(A) - E_a/RT$$

And $k = r \times |\text{HCl}|^n$ where n is the order of the reaction, we obtain:

$$\ln(r) = \ln(A) - E_a/RT - n \ln(|\text{HCl}|)$$

where r is the % change of weight per minute:

$r = (w_i - w_{i-1}) / (t_i - t_{i-1})$, being w the weight of the polymeric sample in milligrams and t is the time in minutes.

A – kinetic constant

E_a – activation energy, in J/mol

R – gas constant, J/mol.K

T – absolute temperature in Kelvin

n – order of the reaction

$|\text{HCl}|$ - concentration of HCl in PVC sample, during the experiment, in weight %.

$|\text{HCl}|$ has been calculated at each time assuming that all the decomposition product is HCl according to the reaction $\text{C}_2\text{H}_3\text{Cl} \rightarrow \text{HCl} + \text{C}_2\text{H}_2$.

With all the experimental data obtained a multivariate regression of $\ln(r)$ has been performed in function of $1/T$ and $\ln(|\text{HCl}|)$. A very good fit has been obtained for all experimental points obtained after the desired temperature has been reached, except for the experiments up to 400 °C. In these ones decomposition rate is much higher than expected, a bad fit being obtained by the model. However, points obtained during heating cycle, until the temperature of 340 °C gives a good fit with the proposed model. For this reason, kinetic model has been calculated just for points where temperature was lower than 340 °C.

The obtained model is:

$$\ln r = 31,3 - 16100/T + 1,020 \ln C(\text{HCl}), r^2 = 0,9912$$

This allows considering that reaction is a first order reaction with activation energy of 133800 J/mol \pm 760 J/mol.

A factorial plan was carried out with different temperatures, performed in laboratory, where the reaction of the thermal decomposition of PVC occurred in a glass tube heated by electrical resistance. The chlorine released, was collected by bubbling on water, in the form of hydrochloric acid. Best results were obtained at the temperature of 340 °C, as shown by the kinetic study.

CONCLUSIONS

In this work, the kinetics of the reaction of thermal decomposition of PVC was studied, leading to the development of the kinetic model, with the expression $\ln r = 31,3 - 16100/T + 1,020 \ln C(\text{HCl})$.

This model was obtained for decomposition temperatures lower than 340 °C, in which almost all chlorine is removed from the pure PVC through the chemical reaction described, with an activation

energy of 133800 J/mol, value very close to the one obtained in others works reported (Ma *et al.* 2002). Considering the results obtained in this work, future experiments will be conducted addressing the de-chlorination of PVC-containing waste, in order to proceed with the gasification of de-chlorinated fraction. Following goal is to produce a synthesis gas with high energetic potential, which could be used in turbines or gas engines, replacing the ones obtained from fossil fuels.

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