



Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Development of a microwave thermogravimetric analyzer and its application on polystyrene microwave pyrolysis kinetics

Philippe Leclerc^a, Jocelyn Doucet^b, Jamal Chaouki^{a,*}^a Dept. of Chemical Engineering, École Polytechnique de Montréal, PO Box 6079, Succ. Centre-ville, Montréal, QC H3C 3A7, Canada^b Pyrowave Inc., 9500 Meilleur, Suite 601, Montréal, QC H2N 2B7, Canada

ARTICLE INFO

Keywords:

Microwave
Thermogravimetric analyzer
Polystyrene
Kinetics
Pyrolysis

ABSTRACT

To study pyrolysis kinetics inside a microwave environment, a microwave thermogravimetric analyzer was developed. A sample mass as low as 0.3 g can be studied along with silicon carbide as the microwave receptor. The temperature is measured with a custom-made infrared thermopile equipped with different optical filters specific to this application. Validation of the microwave thermogravimetric analyzer features showed that the measured data can be used as is for kinetic development. Different heating profiles can be achieved by modulating the microwave power. The microwave thermogravimetric analyzer was then used for the kinetic development of polystyrene microwave pyrolysis. Polystyrene was chosen because of its low recycling rate and its great potential to produce high-valued products, like styrene. Three heating rates (24.5, 38.5 and 49.5 °C min⁻¹) were used to estimate the kinetic parameters. By comparing several reaction models, a random scission model was found to best explain the experimental data. The choice of the reaction model was made based on two statistical tests: the coefficient of determination R^2 and the residual sum of squares RSS. With this reaction model, an activation energy of $E = 45 \text{ kJ mol}^{-1}$ and a pre-exponential constant of $\ln(A) = 3.6$ were found for polystyrene microwave pyrolysis.

1. Introduction

In 2013, the United States generated 2.3 million tons of waste polystyrene (PS) of which only a mass fraction of 1.3% was recovered [1]. The principal reason for this low recovery rate is the incapacity to reprocess the plastic waste in such ways that the output can be reused in virgin plastic applications, such as the production of food and beverage containers and other consumer goods [2]. In fact, actual recycling techniques for polystyrene waste are mostly mechanical, also known as primary and secondary recycling [3]. These recycling techniques include washing, drying, compressing, melting, and molding of the polystyrene waste [4], and most importantly, the waste should not be contaminated [5,6].

Among other recycling techniques, conventional pyrolysis [7,8], and recently microwave (MW) pyrolysis [9], can be applied to recycle polystyrene waste. Pyrolysis is a tertiary recycling technique also known as chemical recycling [3]. The major difference between microwave pyrolysis and the other conventional pyrolysis processes is the heating mechanism. In microwave pyrolysis, the energy is transferred on a volumetric basis, whereas in other conventional approaches the heating occurs on a conduction/convection basis [10]. Unlike primary

and secondary recycling techniques, pyrolysis can handle contamination in the feedstock [11]. Applied to polystyrene, it produces styrene monomers as the major reaction product [12,13]. This recycled styrene can then be reintroduced into the existing ecosystem of refining and polymerization industries [14] and produce any type of goods, including food grade compliant applications. However, other chemicals, like benzene, toluene, ethylbenzene and α -methylstyrene, are produced. Depending on the reaction conditions, styrene yield can go from a mass fraction as low as 0.6% [15] to a mass fraction of 60.6% [16]. Without a proper understanding of microwave pyrolysis reaction kinetics, styrene yield optimization is, and will continue to be, on a trial and error basis.

The first step in pyrolysis kinetic modeling would be the study of the material decomposition kinetics. As pyrolysis produces mainly volatile and some residual carbon at the expense of the mass loss of the material [17], thermogravimetric analysis is thus best suited for its kinetic analysis [18]. Thermogravimetric analysis is a method that measures the mass of a sample as a function of time and temperature using different temperature programs in a controlled environment [19]. It is usually done in a conventional thermogravimetric analyzer (TGA) [20] and most recently in a fluidized-bed TGA [21].

As for microwave pyrolysis, only a few fundamental studies on

* Corresponding author.

E-mail address: jamal.chaouki@polymtl.ca (J. Chaouki).<https://doi.org/10.1016/j.jaap.2018.01.008>Received 29 September 2017; Received in revised form 7 January 2018; Accepted 9 January 2018
0165-2370/ © 2018 Elsevier B.V. All rights reserved.

Table 1
Microwave thermogravimetric analyzers in the literature and their problematic features.

Reference	Problematic features and comments
Ludlow-Palafox and Chase [26]	4 g of HDPE and toothpaste tube were studied in 60 g of carbon as microwave receptors. This amount of microwave receptor is likely to form temperature gradients within the bed. Temperature was measured with only 1 thermocouple, which is probably not representative of the whole temperature.
Song et al. [27]	Bales of corn stalk and wheat straw with dimensions of 1 m × 0.6 m × 0.6 m were studied. With these dimensions, temperature gradients inside the sample are certainly present. Temperature was measured with 5 thermocouples and the average was taken which indicates the non-uniformity of the temperature. Mass loss experiment and temperature measurement experiments were carried out separately and the data were merged afterwards. This method cannot be done inside a microwave cavity because of the <i>thermocouple effect</i> [31].
Sun et al. [32]	40 g of printed circuit board particles with dimensions of 1 cm × 1 cm were studied. This sample mass is large and temperature uniformity should be verified. Temperature was measured with 2 thermocouples: one was continuously monitoring the temperature of the gases and another was inserted in the reactor bed at different intervals while the microwave power was turned off. The latter was used to correct the former. Sparks were observed during the reaction which indicates areas of different temperatures.
Dong and Xiong [23]	50 g of bamboo sawdust with a dimension of 0.38–0.83 mm was studied. While particle dimensions seem adequate for kinetic purposes, the sample mass is large and temperature uniformity should be validated. Temperature was measured with 2 thermocouples and the average was taken, which indicates the non-uniformity of the temperature.
Song et al. [28]	30 g of tire powder with a dimension of 0.45 mm were studied. While particle dimensions seem appropriate for a kinetic study, the sample mass is large and temperature uniformity should be validated. Temperature was measured with only 1 thermocouple, which is not representative of the reaction temperature, especially if there are temperature gradients.
Luo et al. [25]	Pine wood sawdust particles with dimensions of 10–20 mesh were studied. While particle sizes are small, the authors give no information as to the mass of the sample. The temperature was measured with an infrared thermometer. Without proper tuning, infrared thermometer will induce a lag in temperature measurements and therefore precautions must be taken [33].

kinetics have been made and they showed that the pre-exponential constant [22–24] and the activation energy [22,23,25] in the Arrhenius equation were different between microwave and conventional pyrolysis. Those results were obtained in different custom-made microwave TGA [22–28]. They were all designed on the principles of a conventional TGA but unfortunately some important recommendations made by the ICTAC Kinetics Committee on the collection of experimental data for thermal analysis [29], mostly related to temperature measurement, were not considered. First of all, the temperature readings must be of the sample and not of the environment. Then, the particle size must be small enough so that the temperature is uniform throughout the particles. Finally, the sample size must be small enough so that the temperature is uniform throughout the reactor. With microwave heating, particle and sample size is important as a temperature gradient will arise if they are too big [30]. Therefore, improper choice of temperature measurement, particle size and sample size will ultimately lead to false kinetic parameter estimation and thereby wrong conclusions. Table 1 shows a review of the microwave thermogravimetric analyzers that have been developed in the literature along with their features that go against the previous ICTAC recommendations.

Farag and Chaouki also developed a microwave TGA to study pine wood sawdust pyrolysis kinetics [24]. The mass of sawdust in each experiments was 5 g. The authors simulated and validated the temperature gradient inside the reactor and they took it into consideration in the kinetic development.

This paper aims to develop an accurate microwave TGA based on the aforementioned remarks. Features and validations of the microwave TGA apparatus will be presented. A kinetic study of polystyrene decomposition as a post-consumer plastic waste will also be presented.

2. Materials

2.1. Materials

The model material was clear polystyrene beads from Total Petrochemicals & Refining USA, Inc. The beads were first frozen with liquid nitrogen and then crushed with an industrial blender. The resulting polystyrene powder was sieved and the fraction between 300 and 500 μm was kept for all experiments. Green silicon carbide particles (SiC – mean size diameter of 500 μm) from Electro Abrasives LLC were used as the microwave receptor.

2.2. Material characterization

Elemental analysis was done on the polystyrene with an EA3000 elemental analyzer from EuroVector (Table 2). The analysis was done using 3 distinct methods: one for CHN, one for S and one for O. Theoretical C/H ratio for polystyrene is 12. Based on the elemental analysis, the studied polystyrene had a C/H ratio of 11.3–11.8 which means that it was rather pure. This was to be expected since the polystyrene did not come from wastes but from a pure source. The small amount of nitrogen found in the results probably comes from an intake of air during the injection. Proximate analysis was done on polystyrene with a Q5000 thermogravimetric analyzer from TA Instruments (Table 2). The proximate analysis was separated into three steps and based on TA Instruments proximate analysis procedure TA-129. (1) The TGA oven was held at 200 °C for 20 min under nitrogen. (2) The TGA temperature was increased to 900 °C and held for 30 min under nitrogen. (3) Remaining at 900 °C, nitrogen was switched to air for 5 min. The mass losses following the 3 different steps respectively represent the moisture, the volatile and the fixed carbon content. The remaining mass at the end of the analysis represents the ash content. The proximate analysis of polystyrene showed that 100% of the mass is volatile and can be pyrolyzed into condensable and non-condensable gases.

In microwave pyrolysis, receptors play the role of thermal catalyst by acting as the main thermal source to the sample. In some cases, receptors can also have the role of chemical catalyst, like activated carbon [34]. To make sure that the SiC used in this study did not have any catalytic role that could be used as a bias against the kinetic results, polystyrene conventional pyrolysis experiments were done using green SiC as an additive. Results showed that the SiC does not have any effect on the pyrolysis products and therefore plays only the role of thermal catalyst.

Table 2
Elemental and proximate analysis of polystyrene. The error is the standard deviation over 5 experiments.

Elemental analysis		Proximate analysis	
C	91.86 (± 1.14)	Moisture	–
H	7.97 (± 0.26)	Volatile	100.00 (± 0.00)
N	0.36 (± 0.21)	Fixed carbon	–
S	–	Ash	–
O	–		

Download English Version:

<https://daneshyari.com/en/article/7606449>

Download Persian Version:

<https://daneshyari.com/article/7606449>

[Daneshyari.com](https://daneshyari.com)