CHEMICAL ENGINEERING TRANSACTIONS, Volume 11, 2007
Edited by Sauro Pierucci
Copyright © 2007, AIDIC Servizi S.r.l., ISBN 978-88-95608-00-6

Mixtures of tyres and plastics wastes kinetics

Miguel Miranda[a], Filomena Pinto[a], Ibrahim Gulyurtlu[a], Isabel Cabrita[a], Arlindo Matos[b]
[a] INETI-DEECA, Estrada Paço Lumiar, 22, 1649-038 Lisboa, Portugal
[b] UA, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

In modern societies tyres and plastics have been extensively used producing increasing amounts of wastes with negative impact on environment. Pyrolysis technology applied to these wastes could be an alternative source of fuels and raw materials for several industries, allows the conversion of these residues into economical valuable hydrocarbons. A waste mixture with 20% (w/w) of PE, 30% (w/w) of PP, 20% (w/w) of PS and 30% (w/w) of tyres residues was used. Previous studies based on Response Surface Methodology (RSM) led to the following optimized experimental conditions: 0.48MPa, 370°C and 15 minutes reaction time. Results obtained, based on liquid maximization were 5% gas, 13% solid and 82% liquid, which were analysed using GC-MS to identify the main compounds. Kinetics studies found in literature are based on Thermal Gravimetric Analysis (TGA) measurements which only consider weight loss. Therefore these models are very simple approached to reality. In the present work is presented a more complete kinetic study using small batch reactors (0.16L) to identify possible reaction routes in waste mixture using different temperatures and reaction times considering the formation of gases, liquids and solids. A kinetic model was proposed and activation energy, reaction rates and pre-exponential factors were calculated.

1. Introduction

Tyres and plastics wastes are continuously growing creating environmental problems in most develop countries. Therefore is vital the implementation/development of processes in order to promote wastes valorisation, in an energetic point of view as well as recovery their organic content. Several thermal cracking technologies have been used to study this kind of wastes. Pyrolysis thermal decomposition allows the conversion of tyres and plastics wastes into economical valuable products; under moderate conditions of temperature and pressure Pinto (1999), though pyrolysis wastes polymeric structure is broken down producing smaller intermediate species, which can further react and produce a mixture of smaller hydrocarbon molecules, being liquid and gas in nature which may be used as fuel or as raw material in several industries. Product distribution obtained for 420°C, 0.41MPa and reaction time 30 minutes was a mixture of liquid hydrocarbons, whose yields changed between 62 and 67% (w/w). Gases yields were lower than 12% (w/w), whilst the residual solid obtained varied between 20 and 26% (w/w). TGA measurements were used in most kinetic studies reported in literature, Marcilla (1999). These TGA studies consider that plastics thermal degradation occurs though a random breakdown mechanism following a first order kinetic. In these studies, only sample weight loss is measure therefore, cracking and other chemical reactions not involving weight loss can not be measure. Consequently, these studies are simple approaches to what really append during wastes pyrolysis. In the present work it was used a new approach using series of small batch reactors to quantify the formation of gases, liquids and solids at different reaction times from few seconds (minimum time) till 15 minutes. No information was found in literature using this kind of approach. As a result, it was possible to follow the formation of each product and to detect the effect of reaction time on reactions between products initial formed and their inter-conversion. Major compounds formed were isoprene, 2-5-furanon, ethylbenzene, xylene, cumene, n-butylbenzene, 4-ethyl-2-methoxyphenol, estirene, dipentene and pentacosane whose concentrations varied for the different experimental conditions tested.

2. Experimental Part

Tyres wastes main components were: natural rubber (NR), styrene butadiene rubber (SBR) and butadiene rubber (BR). A mixture with the following composition was selected (w/w): 20% PE, 30% PP, 20% PS and 30% tyres residues. Pyrolysis experiments were carried out in batch reactor whose experimental procedure is described elsewhere, Pinto (2001). Tyres pyrolysis experimental conditions based on Response Surface methodology (RSM) was found to be: 370°C of temperature 0.48MPa of initial pressure, and 15 minutes for reaction time. A complex liquid hydrocarbon mixture was obtained and distillate in three fractions, ASTM standard (1994) (lighter fraction, distillation point lower than 150ºC, second fraction between 150ºC and 270ºC and the third one higher than 270ºC). Liquid fractions were analyzed by GC-MS in order to identify their main compounds, Miranda (2002). Kinetic study was accomplishing using small batch reactors in order to study and quantify the formation of gas, liquid and solid and possible reactions routes were proposed based on different temperatures (350-450ºC) and reaction times varying between 12 to 900 seconds. Each reactor, after load was pressurized to 0.48MPa (nitrogen), heated and being maintained at each temperature study and reaction time previously establish. Subsequently, the reactor was cooled down and gases were measured. Finally, the reactor was opened and its content was weighted; as solids obtained were soaked with liquids, it was necessary to use solvent extraction process, first with dichloromethane and then with tetrahydrofuran to remove all liquids from the solid fraction.

3. Discussion of Results

In previous experiments it was study the influence of several experimental parameters that direct influence liquid formation and establish products sampling techniques and analysis; previous studies, Pinto (1999) and Pinto (2001) p. 363-370, allowed selecting experimental conditions. The use of RSM applied to wastes pyrolysis allowed to optimise experimental conditions based on maximization of liquid production. In order to validate the results, same experiments were conducted sequentially and average yields (w/w) were calculated: 5% gas, 13% solid and 82% liquid. The results obtained at several temperatures allow to propose a kinetic model and also to calculate Ea and pre-exponential factors for the main products formed. The innovation of the present work is based on products quantification obtained (gas, liquid and solid), proposing possible routs for different temperatures and reaction times. The validation of this model will be confirm by the programme Micromath® Scientist® for windows TM, which will solve the differential equations (1) to (5), using Range-Kutta method based on Taylor theorem. If necessary, the proposed model will be adjusted for a better description of experimental results.

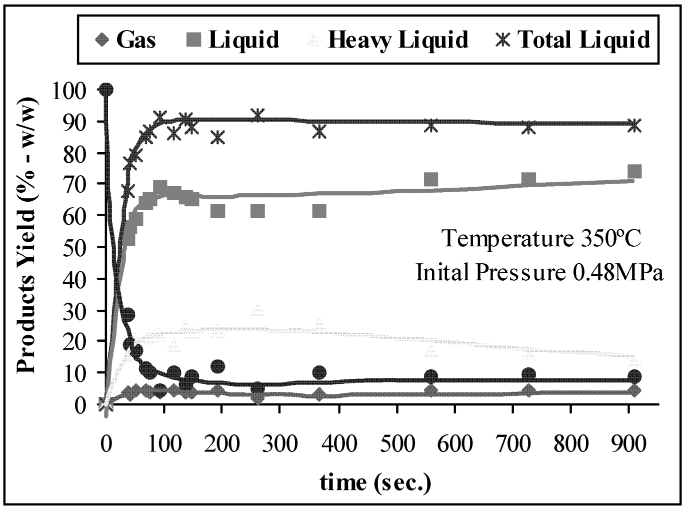

Figure 1 – Effect of reaction time on products yields at 350°C.

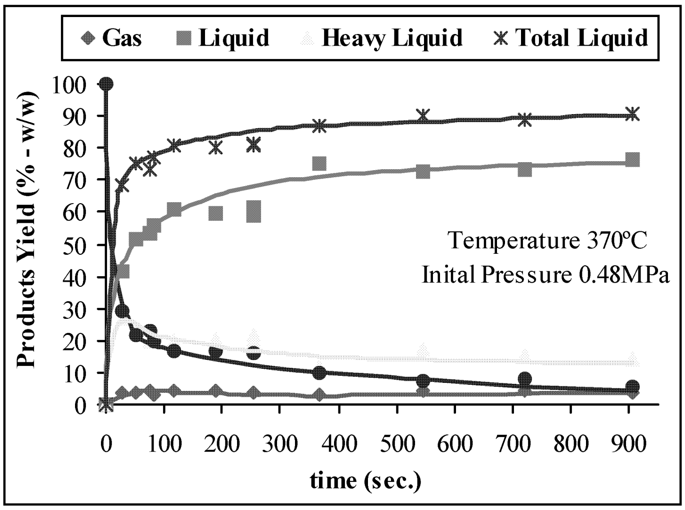

Figure 2 – Effect of reaction time on products yields at 370°C.

It was study the effect of reaction time on products yields at 0.48MPa for temperatures 350°C, 370°C, 390°C, 410°C, 430°C and 450°C. In Figure 1 is presented the effect of reaction time on products yields at 350°C. Solid obtained was submitted to a solvent extraction process, first with dichloromethane (liquid fraction - Liquid) and then with tetrahydrufuran (liquid fraction -Heavy Liquid). The increase in reaction time to values around 150 seconds increased formation of Liquid at expenses of a decrease in solid (reaction k_5). Although, to reaction time higher than 200 seconds, Heavy Liquid were probably converted into Liquid. Both solid and gas yields present a constant behaviour reaching values around 10% (w/w) and 5% (w/w) respectively. In Figure 2 and 3 is presented the effect of reaction time on products yields for a temperature of 370ºC and 390ºC. Similar behaviour was found, although there are some indications that Heavy Liquid star to convert into Liquid for shorter reaction times.

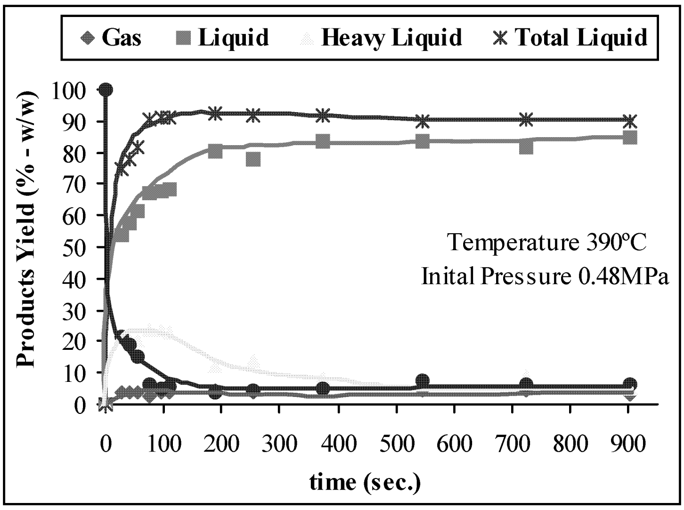

Figure 3 – Effect of reaction time on products yields at 390ºC.

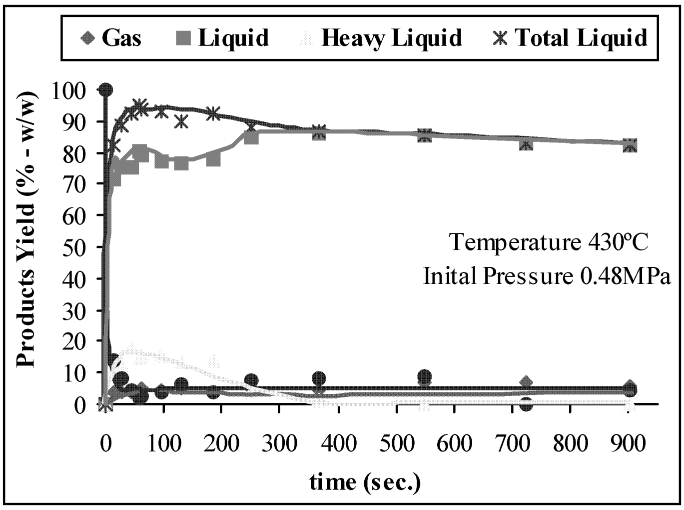

Figure 4 – Effect of reaction time on products yields at 430ºC.

In Figures 4 and 5 is presented the same effect only for the temperatures of 430ºC and 450ºC respectively. In Figure 4 is still possible to identify that the conversion of Heavy Liquids (HL) into lighter liquids (L) still occurred although it started more rapidly and after 380 seconds no more Heavy Liquid seemed to be converted into liquid. Solid and gas seem to present a constant behaviour reaching values around 10% (w/w).

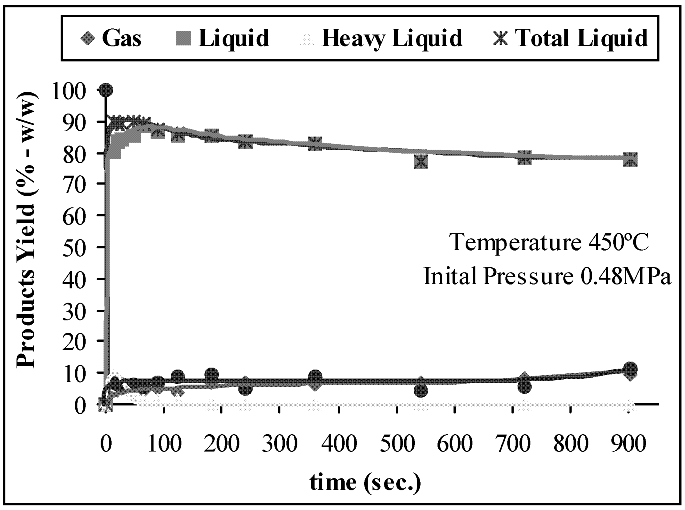

Figure 5 – Effect of reaction time on products yields at 450°C.

The analysis of the results shown in Figures 1 to 5 allowed to propose the kinetic model presented in Figure 6. The proposed model considered that initial product (P) after submitted to thermal degradation was converting into several products such as gas (G) after reaction k_1, liquids such as (L) and (HL) through reactions k_2 and k_3 and a solid (S) through k_4. Based on experimental results of Figures 1 to 5, the model suggests that other reactions take place as some solid (S) is converted into either (L) (reaction k_5) or (HL) (reaction k_7). The conversion of (HL) into (L) (reaction k_6) was also considered. Based on proposed kinetic model, differential equations can be establishing taking in account the product (P) and all sub-products L, HL, S and G:

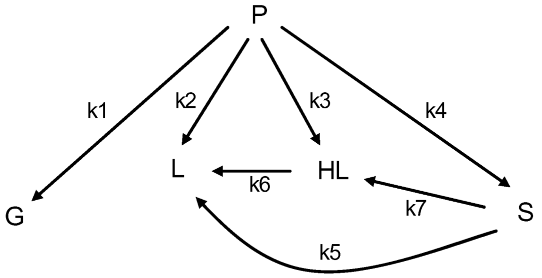

Figure 6 – Pyrolysis kinetics model and possible reaction routs

$\partial P/\partial t = -k_1P - k_2P - k_3P - k_4P$ (1)

$\partial L/\partial t = k_2P + k_5S + k_6HL$ (2)

$\partial HL/\partial t = k_3P - k_6HL + K_7S$ (3)

$\partial S/\partial t = k_4P - k_5S - k_7S$ (4)

$$\partial G/\partial t = k_1 P \quad (5)$$

In Figure 7 is presented the Arrhenius representation for pyrolysis of tyres and plastics wastes using initial reaction rates for the different products obtained. Values for activation energy (Ea) were calculated and found to be: 56.7, 57.5 and 46.0 kJ mol^{-1} for Total Liquid, Liquid and Gas respectively. Pre-exponential factor was also calculated and found to be for Total Liquid 7.2946*10^{10}, Liquid 6.5313*10^{10} and Gas 9.8084*10^{5}.

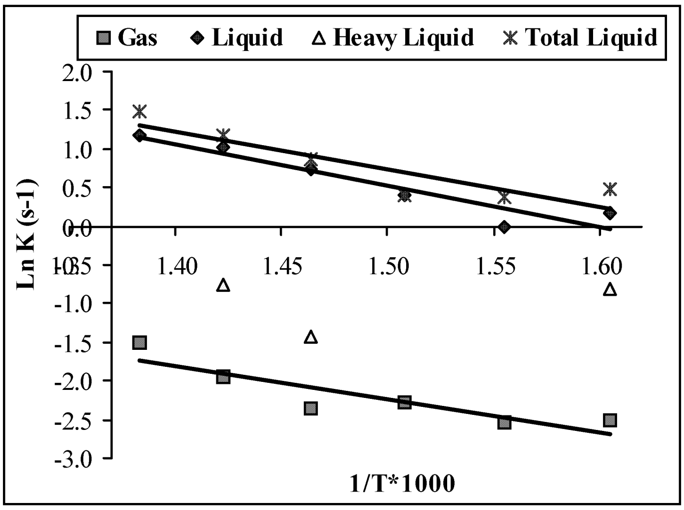

Figure 7 – Arrhenius representation for pyrolysis of tyres and plastics wastes.

4. Conclusions

Pyrolysis of tyres and plastics wastes may play an important role in the future in converting these wastes into valuable products which can be used as fuel or raw material to several industries. The application of RSM in liquid experimental optimization found to be very useful as it allows obtaining higher liquid yield. An innovated method kinetic study was used based in the quantification of gas, liquids and solid products formed during pyrolysis of these wastes at different reaction times and temperatures. A kinetic model was proposed and activation energies, reaction rates and pre-exponential factors were calculated.

5. References

Annual Book of ASTM Standards, (1994), Volumes 05.01 and 05.02.

A. Marcilla, R. Font, J. A. Caballero, J. A. Conesa, "Journal of Analytical and Applied Pyrolysis", 1999, 36, 1-15.

Filomena Pinto, I. Gulyurtlu, Paula Costa, I. Cabrita, "Journal of Analytical and Applied Pyrolysis", 1999, 51, 39-55.

Filomena Pinto, Miguel Miranda, I. Gulyurtlu, I. Cabrita, "Study of Pyrolysis Process to Recycle Tyres and Plastic Wastes", "International Symposium - Recycling and Reuse of Tyres", Dundee, Scotland, p. 27-38, 2001.