

Study of the Slow Batch Pyrolysis of Mixtures of Plastics, Tires and Forestry Biomass Wastes. Effect of the Experimental Conditions in the Liquid Compounds.

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EXECUTIVE SUMMARY

In this work was studied the effect of experimental conditions in the production of liquid compounds from slow batch pyrolysis of mixtures of plastics, tires and pines wastes. The major compounds formed were toluene, ethylbenzene, and linear alkanes from C5 to C10 (each reaching yields around 5% w/w of the initial waste mixture). The pyrolysis reaction time and temperature improved the production of those species, while decreasing heavier alkanes formation. An increase of plastics content in waste mixture seemed to favour the production of lighter alkanes, although this effect was not as notorious as the ones just mentioned. The styrene production decreased regularly with the decrease of tyres content in the mixture. Autoclave initial pressure variation did not seem to affect significantly the formation of the major compounds.

INTRODUCTION

Plastics wastes generation has been increasing all over the years in modern societies. The traditional methods used for these wastes disposal such as incineration and land filling are far from the optimum solution as they pose some environmental issues and the wastes organic content is not properly retrieved. Used tires are another problematic waste stream. Additionally, biomass residues accumulated in forests and posing a risk of fires could be otherwise processed in order to retrieve its organic matter in a useful form.

One viable and promising way of taking profit of all these wastes energetic and of organic content is by pyrolysis.

Pyrolysis study of ternary mixtures is quite a new subject and there is not much information published. The effect of the experimental conditions on slow batch pyrolysis of mixtures of plastics, biomass and tyres residues has been studied by the present authors and the results obtained were already presented in previous publications. It was discussed the effect of experimental conditions in the slow batch pyrolysis of mixtures of plastics and pine in a first stage, Paradela *et al* (2009a) and of plastics, pine and tires in a second stage, Paradela *et al* (2009b).

The average HHV of the obtained gases was 35 MJ/m³. Two immiscible liquid phases were formed in the tests where pine was present, one being mainly water with traces of compounds commonly produced by fast biomass pyrolysis, and the other being a less dense organic phase. The average

HHV of these organic phases was about 40 MJ/kg. The char resulting from the pyrolysis tests showed an average HHV of 34 MJ/kg (daf) and the residue from liquid distillation (solid at room temperature) an average 45 MJ/kg (daf).

It was analyzed the effect of the experimental conditions on the liquid composition and the compounds obtained were grouped in alkanes, alkenes and aromatic compounds. The results obtained showed that the rise of reaction temperature decreased liquid yields, by increasing solids and gases yields and also led to higher alkanes content on the produced gases. On the other hand, the increase of initial pressure did not lead to significant variations in products yields and composition. The increase or pyrolysis reaction time led to a small decrease in liquids formation, favouring the release of alkane gaseous compounds. It also favoured the production of lighter liquid compounds. Plastics content on wastes mixture was the parameter that most affected pyrolysis products and composition. The rise of plastics amounts led to higher liquid yields, and more gaseous alkanes, while CO and CO₂ were the main gaseous products formed when higher pine percentages were used.

In this paper was studied the effect of experimental parameters on the formation of main liquid compounds obtained by the pyrolysis of the ternary waste mixtures.

EXPERIMENTAL

Pyrolysis experiments were conducted in a 1 litre autoclave made of Hastelloy C276 alloy (by Parr Instruments). Detailed information about the pyrolysis installation and experimental procedure was described in a previous paper [Pinto *et al.* (1999)]. Plastics content in the waste mixture was varied from 0% to 100% (w/w) (the difference to 100% in each run was composed by equal parts of pine and tires). Plastic relative composition of 56% PE (polyethylene), 27% PP (polypropylene) and 17% PS (polystyrene) was kept a constant, simulating their distribution in plastics fraction of Portuguese MSW. The following range of experimental conditions was used: pyrolysis temperature: 350 to 450 °C, reaction time: 5 to 30 min and initial pressure: 0.2 to 1.0 MPa. Waste particle size was lower than 3 mm.

The liquid product fraction was distilled according to ASTM D86 [ASTM standards (1994)] and three fractions were obtained: the first one distilled below 150 °C and contained the lightest hydrocarbons, the second distilled fraction had heavier hydrocarbons (150 °C < bp < 270 °C) and the residual one (bp > 270 °C). The first two distillates were analyzed by GC and GC/MS. The distillation curve of the liquid fraction was also compared to the ones of gasoline and diesel, laying between the two. The remaining solid fraction was weighted and extracted with dichloromethane (DCM) and tetrahydrofuran (THF) in a soxhlet extractor according to ASTM D5369-93 [ASTM standards (1994)] to recover the liquids adsorbed in the solid. The dried solid product was weighted to give the effective pyrolysis yield of solids. The extracted liquids were also subsequently analyzed by GC and GC/MS.

The results presented in this paper refer to total liquid yields, also considering liquids removed from the solids by soxhlet extraction.

RESULTS

The effect of the reaction time in the production of aromatic compounds is shown in Figure 1. The major aromatic compounds were always ethylbenzene and toluene while the others appeared in much less quantities. It can be seen that the production of ethylbenzene and toluene appears to increase when the reaction time increased from 15 to 20 minutes, but the further increase to 30

minutes did not seem to result in an appreciable production improvement of these compounds. The use of longer reaction times did not show any noticeable effect in the production of other aromatic compounds.

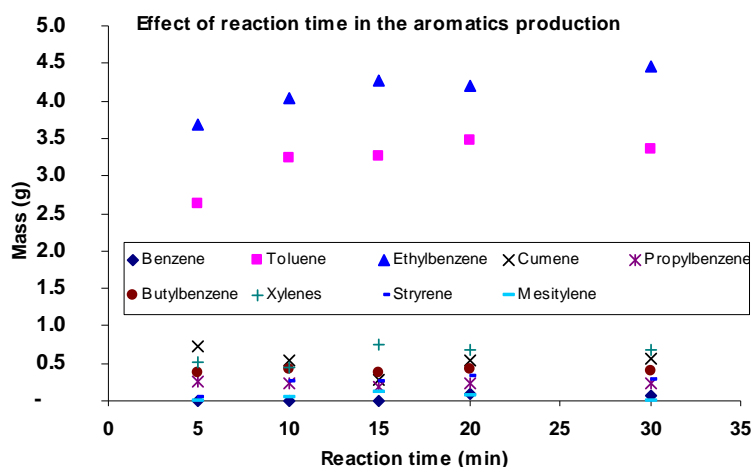


Figure 1: Effect of the reaction time in the production of aromatics compounds. Experimental conditions: reaction temperature: 420 °C, initial pressure: 0.4 MPa and waste mixture composition: 80% plastics, 10% pine and 10% tires.

Figure 2 shows that the use of longer reaction times seems to promote the formation of lighter n-alkanes, especially those up to 10 carbon numbers, whose presence in pyrolysis products obtained for the 5 minutes run is very low. On the other hand, Figure 3 seems to indicate that heavier hydrocarbons (especially those with carbon atoms above 18) are formed in higher amounts in the first stages (lower reaction times) and then decrease as the reaction carries on, possibly being further degraded to smaller fragments for longer reaction times. It can also be seen in the two figures that intermediate alkanes (ranging from 13 to 17 carbon atoms) seem to maintain a near constant production throughout the various reaction times. This can be due to the fact that these compounds are constantly formed by decomposition of heavier alkanes, which replace the ones being converted into lighter hydrocarbons, thus keeping the overall final production nearly constant.

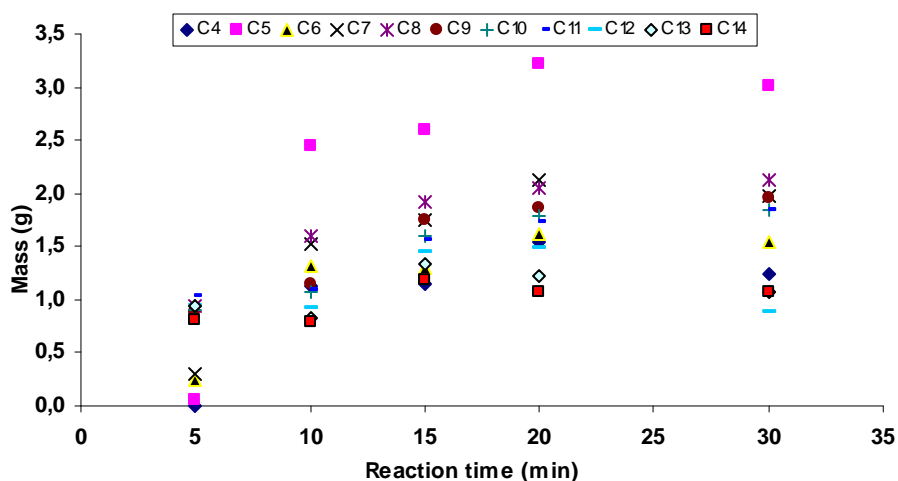


Figure 2: Effect of the reaction time in the production of lighter alkane compounds. Experimental conditions: reaction temperature: 420 °C, initial pressure: 0.4 MPa and waste mixture composition: 80% plastics, 10% pine and 10% tires.

Costa (2006) and Lee and Shin (2007) obtained similar results in their works, although only plastic

mixtures were used. It was not found in the literature similar works with mixtures of pine, tires and plastics, so it was not possible to compare the results obtained with other obtained by other researchers.

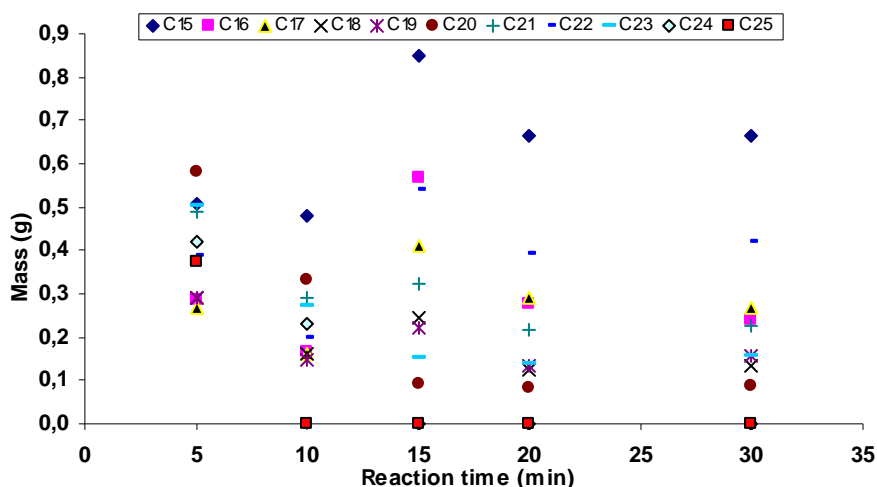


Figure 3: Effect of the reaction time in the production of heavier alkane compounds. Experimental conditions: reaction temperature: 420 °C, initial pressure: 0.4 MPa and waste mixture composition: 80% plastics, 10% pine and 10% tires.

Figure 4 shows the effect of the reaction temperature in the production of aromatic compounds. The major compounds were again ethylbenzene and toluene. The production of ethylbenzene seemed to reach the maximum value at 380°C, remaining constant when higher temperatures were used. On the other hand, the production of toluene seemed to increase in an almost linear trend with the temperature increase. The rise of the temperature reaction also led to higher production of xylenes and styrene, while the other aromatics compounds did not seem to be affected in a clear way.

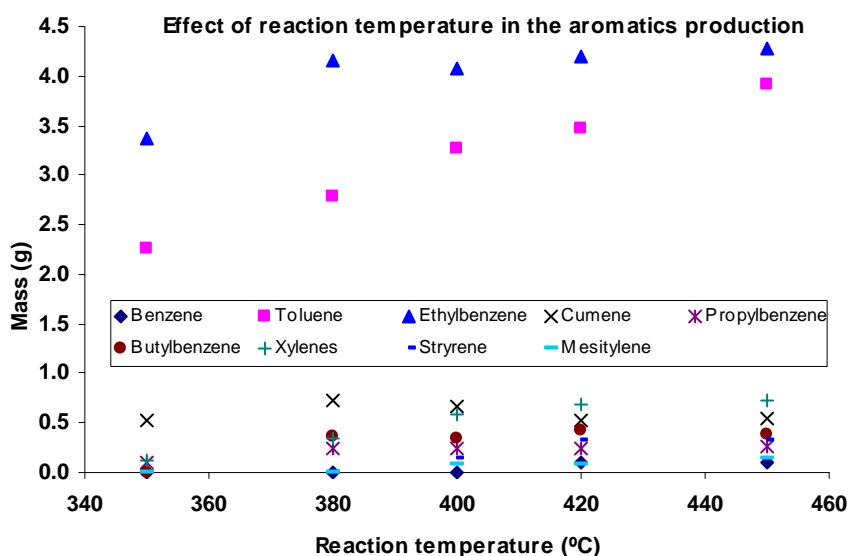


Figure 4: Effect of the reaction temperature in the production of aromatics compounds. Experimental conditions: reaction time: 20 minutes, initial pressure: 0.4 MPa and waste mixture composition: 80% plastics, 10% pine and 10% tires.

Pinto *et al.* (2001) observed an increase in the production of toluene, ethylbenzene and propylbenzene when temperatures higher than 400 °C were used in the pyrolysis of mixtures of plastics and tyres.

From the observation of Figure 5, it seems that the rise of the pyrolysis temperature promoted the formation of lighter n-alkanes, while its effect on the heavier ones is not so clear (Figure 6). That trend seems to continue for alkanes up to C18, while for those with carbon atoms from C18 to C24 there seems to be a maximum production at 400°. This effect might be due to the cracking of these longer hydrocarbons into smaller at higher temperatures.

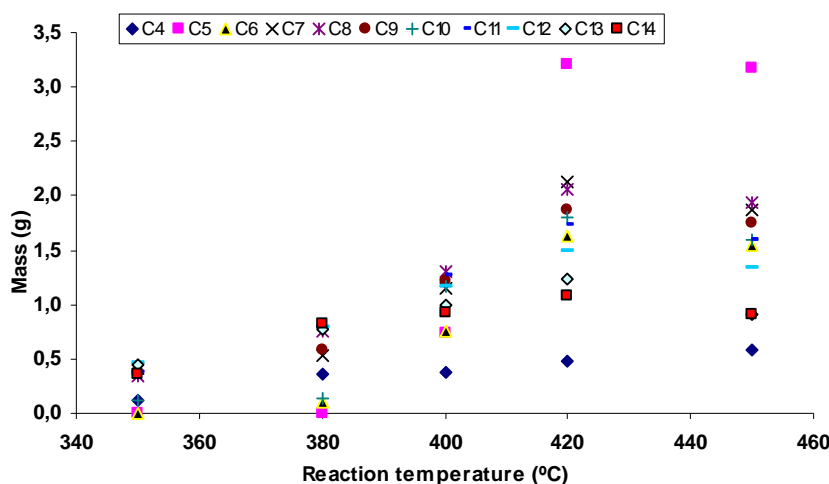


Figure 5: Effect of the reaction temperature in the production of lighter linear alkanes. Experimental conditions: reaction time: 20 minutes, initial pressure: 0.4 MPa and waste mixture composition: 80% plastics, 10% pine and 10% tires.

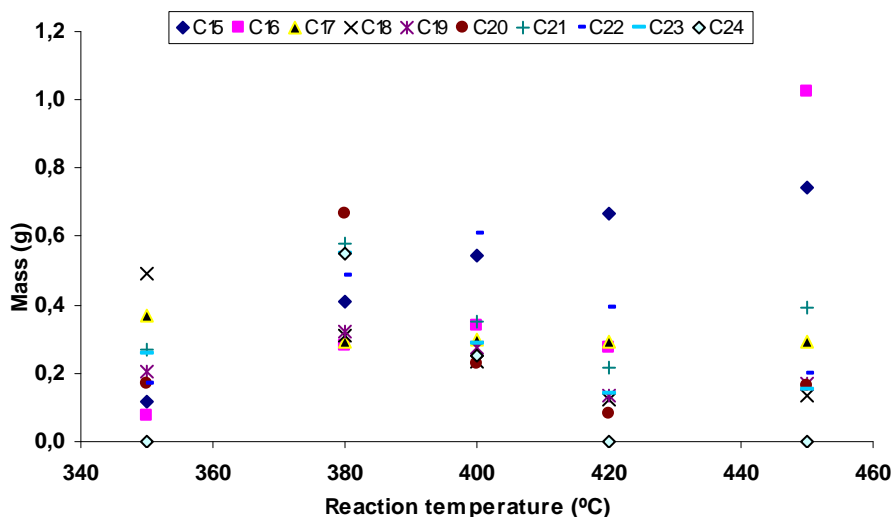


Figure 6: Effect of the reaction temperature in the production of heavier linear alkane compounds. Experimental conditions: reaction time: 20 minutes, initial pressure: 0.4 MPa and waste mixture composition: 80% plastics, 10% pine and 10% tires.

In Figure 7 it can be seen that the initial nitrogen pressure did not seem to influence the production of aromatic compounds. The higher production values observed at 0.4 MPa might be due to experimental deviations, since they clearly stand out of an almost constant production trend when

all the other pressures were employed.

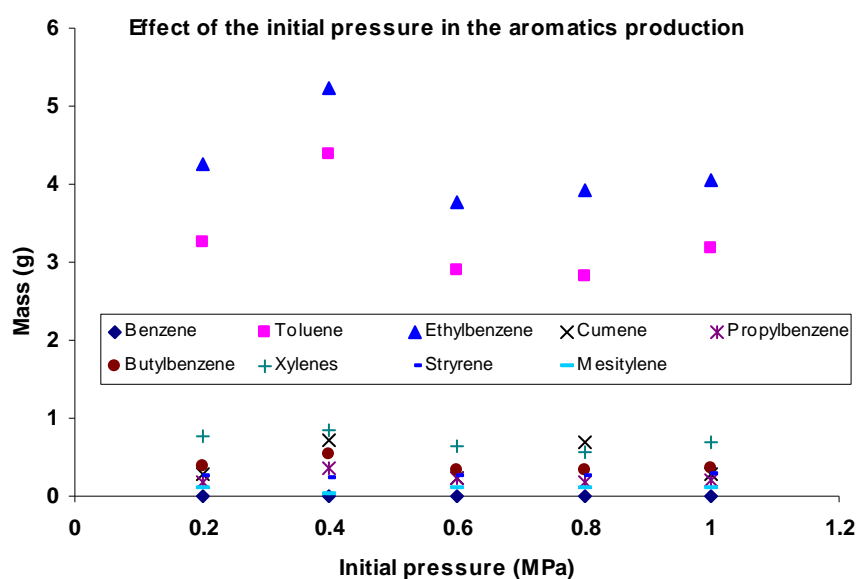


Figure 7: Effect of the initial pressure in the production of aromatics compounds. Experimental conditions: reaction temperature: 420°C, reaction time: 20 minutes and waste mixture composition: 80% plastics, 10% pine and 10% tires.

The effect of the initial nitrogen pressure in the production of linear alkanes was not completely clear. However, with the exception of pentane, it seems that the increase of the pressure did not lead to substantial changes in the production of the lighter alkanes (Figure 8), while in the heavier ones a higher production is again noticed when the pressure of 0.4MPa was used (Figure 9).

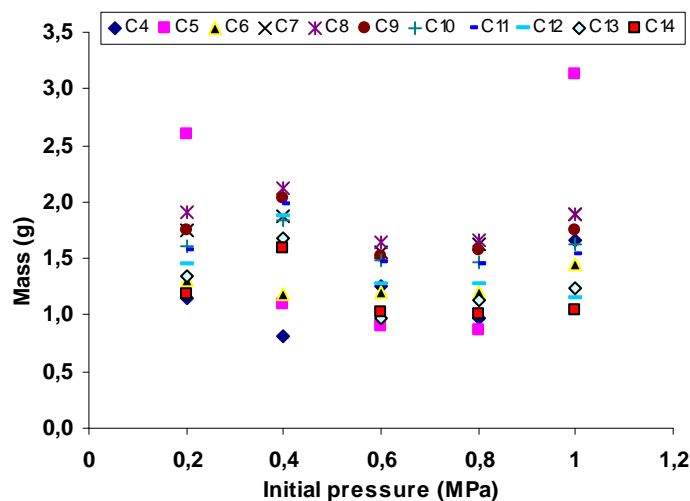


Figure 8: Effect of the initial pressure in the production of lighter linear alkanes. Experimental conditions: reaction temperature: 420°C, reaction time: 20 minutes and waste mixture composition: 80% plastics, 10% pine and 10% tires.

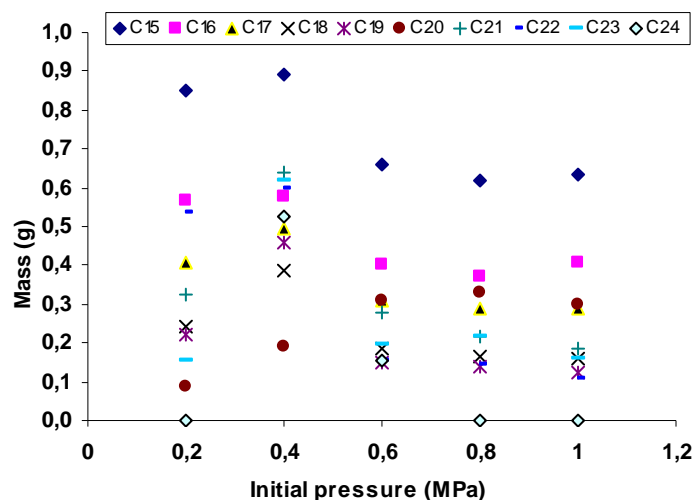


Figure 9: Effect of the initial pressure in the production of heavier linear alkanes. Experimental conditions: reaction temperature: 420°C, reaction time: 20 minutes and waste mixture composition: 80% plastics, 10% pine and 10% tires.

Figure 10 shows that the plastics content in the initial waste mixture was the experimental parameter that showed the greatest effect on aromatic compounds production. Styrene was the major aromatic compound when only tyres were pyrolysed, probably due to chemical structures of tyres main compounds, but its production decreased in a regular way when the plastics content increased (and therefore the tyres content decreased), which agrees with plastic wastes composition, as the PS was the polymer used in lower amount. Xylenes were also produced in higher quantities when only tyres were used. Toluene and ethylbenzene both rose when the plastics content was increased. In the run done with 100% pine pyrolysis those compounds were also formed in appreciable amounts.

The formation of lighter linear alkanes was favoured by the increase of the plastics content in the waste mixture, which also favoured overall liquids formation. The formation of lighter linear alkanes seemed to reach a maximum for the pyrolysis run with the 80% plastics, 10% tires and 10% pine mixture (Figure 11). The effect on heavier alkanes is less clear, although a lower formation of alkanes with carbon atoms higher than C20 seemed to have occurred (Figure 12).

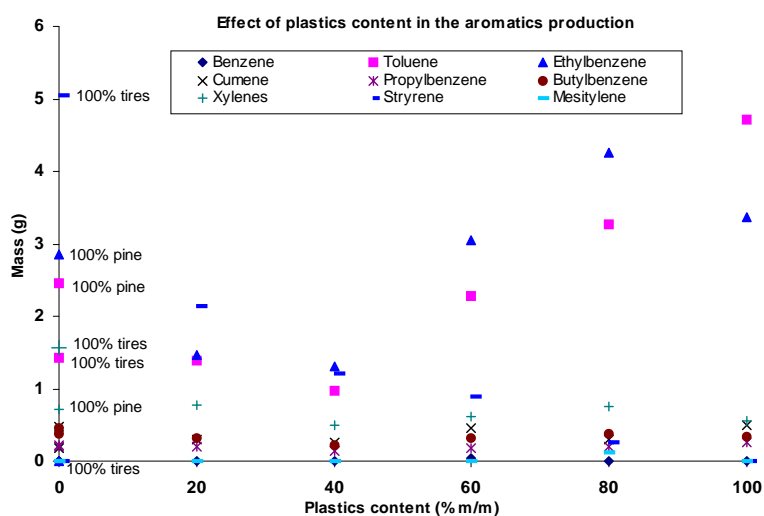


Figure 10: Effect of the plastics content of the waste mixture in the production of aromatics compounds. Experimental conditions: reaction temperature: 420°C, reaction time: 20 minutes and initial pressure: 0.4 MPa.

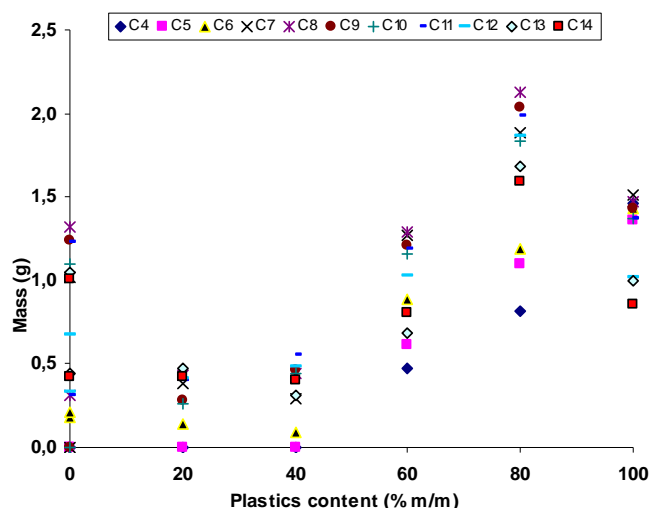


Figure 11: Effect of the plastics content of the waste mixture in the production of the lighter linear alkanes. Experimental conditions: reaction temperature: 420°C, reaction time: 20 minutes and initial pressure: 0.4 MPa.

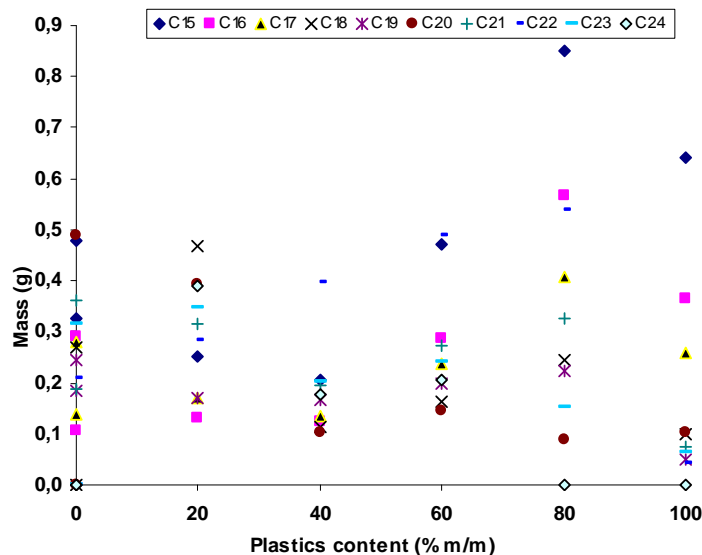


Figure 12: Effect of the plastics content of the waste mixture in the production of the heavier linear alkanes. Experimental conditions: reaction temperature: 420°C, reaction time: 20 minutes and initial pressure: 0.4 MPa.

CONCLUSION

The compounds formed in more amounts in the majority of the trials were toluene, ethylbenzene, and linear alkanes from C5 to C10.

The experimental conditions that most affected the formation of the studied compounds were: pyrolysis reaction time and temperature and plastics content in wastes mixture.

Pyrolysis reaction time improved the production of lighter alkanes, toluene and ethylbenzene, although the rise from 20 to 30 minutes did not seem to produce substantial improvement in their formation. On the other hand, heavier alkanes production was decreased with longer reaction times.

The pyrolysis reaction temperature also improved ethylbenzene, toluene and lighter saturated hydrocarbons and decreased heavier ones production, exhibiting thus a similar effect to the reaction time.

An increase in the plastics content of the mixture seemed to have favoured the production of lighter alkanes, although this effect was not as notorious as the ones just mentioned. The rise of plastics content from 80% to 100% decreased the formation of some of these species. Toluene and ethylbenzene production was favoured by the rise of plastics content, but these species were also formed when 100% pine was pyrolysed. The styrene production decreased regularly with the decrease of tires content in the mixture.

The initial nitrogen pressure did not produce a clear effect in the formation of the studied compounds and they seemed to be unaffected by an increase in the autoclave starting pressure.

The hypothesis formulated in this paper will be validated in a future work by kinetic studies, which are expected to provide a better understanding of pyrolysis reactions and the inter-conversion between the liquid compounds.

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