



Upgrading of chlorinated oils coming from pyrolysis of plastic waste



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ABSTRACT

The objective of this paper is the upgrading of chlorinated oils coming from the pyrolysis of mixed plastic waste, in order to use them as fuel or feedstock for refineries. Two different samples of pyrolysis oils have been thermally and catalytically cracked in a 300 mL autoclave at 325 °C and the auto-generated pressure. Thermal cracking converts the plastic pyrolysis heavy oils into light liquid fractions which are only composed of alkanes and aromatics. These light fractions present a very low quantity of chlorine compared to the initial oils and resemble gasoline and diesel-like products. Besides, a gaseous fraction rich in methane and with very high heating value is also produced, together with a fuel-like viscous product which remains in the autoclave. The relative proportions of each of these three fractions depend on the nature of the initial oils. Red Mud has proved to be a dehydrochlorination and cracking catalyst, since it gives rise to higher quantity of gases and light liquid fractions with a very low chlorine content (<0.1 wt.%). Therefore, dechlorinated light oils can be obtained by Red Mud low temperature catalytic cracking of plastic derived chlorinated pyrolysis oils.

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1. Introduction

Pyrolysis of plastic waste has been intensively studied over the last few decades with the objective of producing useful liquid and gaseous fuels or chemicals from low value polymeric waste [1–6]. Scientific literature claims that pyrolysis could be used to valorise the plastic fraction of municipal and industrial solid waste; however, many of the industrial or demonstration processes implemented in the last years no longer run nowadays [7,8]. The difficulty to find market applications for the pyrolysis derived liquid product seems to be the handicap stopping the current development of the plastic waste pyrolysis process, since the process itself is by now a well-known technology for a while and there are normally no technical problems in its implementation.

The liquid fraction obtained by pyrolysis of plastic waste presents good properties for application as fuel or chemical feedstock for refineries: they are hydrocarbon oils with high calorific value and high carbon content, and free of water provided that the quantity of impurities as paper or wood is not very high in the original sample (<8 wt.%) [9,10]. On the other hand, the typical drawbacks of this liquid fraction are the broad carbon-range distribution (C5–C25 or higher) and the presence of different functional groups and families of organic compounds (mainly aromatics, olefins and alkanes) [11,12]. The balance between advantages and drawbacks of the pyrolysis oils depends on the initial waste sample composition and on the process characteristics. In fact, some authors claim that when pure polyethylene (PE) and polypropylene

(PP) are pyrolysed under specific conditions, the obtained liquids can be directly used as feedstock for fluid catalytic cracking (FCC) units of petroleum refineries, as an alternative to vacuum gas oil [13,14].

Unfortunately, it is very difficult to obtain a liquid fraction with a direct industrial application when it comes to complex plastic mixtures such as municipal plastic waste, since such mixtures contain many materials intermingled with PE and PP, among others, polystyrene (PS), poly(ethylene terephthalate) (PET) and halogenated polymers like poly(vinyl chloride) (PVC) [9,10,15]. In such cases, the liquid fraction presents additional drawbacks for direct application, hindering the implementation of a large scale pyrolysis process for municipal plastic waste. Some of these drawbacks are mainly the presence of chlorine [16] and sometimes the waxy (semi-solid) nature of this product, which complicates its handling and processing [17]. Previous works carried out by the authors indicated that these undesirable properties can be partially overcome in the pyrolysis process itself, e.g., by using catalysts to shorten the carbon-range and/or to avoid the formation of waxy liquids [18], or by stepwise pyrolysis (two step pyrolysis) to reduce the chlorine content [16].

These works proved that a two-step process consisting of a first step at around 300 °C and a second one around 500 °C is the best option in order to obtain pyrolysis oils with very low content of chlorine, but the obtained liquids remain their waxy appearance [16]. On the contrary, every time a single step process has been carried out in presence of a catalyst or a chlorine adsorbent (Red Mud, ZSM-5 zeolite, CaCO₃, mixed with the sample), fluid pyrolysis liquids have been obtained, but the chlorine content of the oils were much higher than those obtained in the two step process, and even higher than the oils obtained in a single step pyrolysis without catalyst [18]. Additionally, a catalytic two-step process was also proved by the authors and fluid pyrolysis

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oils with lower chlorine content than those obtained in the catalytic single process were produced, but their chlorine content was still a little bit higher than in the case of the two-step process without catalyst [19]. Therefore, “offline upgrading” arises as an unavoidable step in order to obtain short carbon chain dechlorinated liquids.

There is here a challenge for scientific community since the final step for the utilization of plastic derived pyrolysis oils seems to be very close, but surprisingly, quite little work is found in literature concerning this topic. This fact becomes even more surprising when compared to the work carried out in the upgrading of biomass pyrolysis liquids (bio-oils), taking into account that, at first sight, the technical drawbacks concerning the potential application of bio-oil as a liquid fuel or feedstock for refineries are quite more difficult to overcome than the aforementioned for the plastic pyrolysis liquids, since bio-oils are instable, corrosive and high oxygen containing organic compounds, always mixed with water to a greater or lesser extent [20,21].

The majority of published papers concerning the upgrading of plastic pyrolysis liquids has been carried out with PE/PP pyrolysis derived liquids [22–27]. In such works, distillation [22,23], thermal and catalytic cracking [24–26] and the combination of both [27] have been studied. The main conclusions which can be drawn from these papers are that (1) cracking is an adequate solution to upgrade pyrolysis oils, mainly by shortening the carbon-range and converting the waxy products into lighter ones through chemical reaction and (2) distillation is an effective way to separate the pre-cracked oil, but not to obtain useful fractions if it is the unique operation used.

Cracking is also the selected process not only for the upgrading of PE/PP derived liquids, but also for pyrolysis oils coming from chlorine containing complex mixtures of plastics. With this type of sample, and as far as the authors know, only some research works carried out by Lingaiah et al. [28,29] and Miskolczi et al. [30] have been published. Miskolczi et al. [30] proposed a two stage process consisting of a first thermo-catalytic cracking using acid catalysts and a second stage with nickel and cobalt-based catalysts. Quite large molecules (larger than C20) still remained in the final liquid product, but they achieved an important reduction of chlorine content. On the other hand, the work of Lingaiah et al. [28,29] was focused on the catalytic activity of iron-based catalysts in order to dehydrochlorinate the pyrolysis oils. They showed the potential of iron oxide to dechlorinate pyrolysis oils but they did not observe any considerable change in the carbon number distribution. In conclusion, it seems that an integral upgrading of chlorine containing pyrolysis oils (chlorine removing and carbon-range shortening) has not been achieved up to now.

For this reason, the objective of the present work was to upgrade chlorinated pyrolysis oils in terms of both dechlorination and chemical transformation, shortening the carbon number distribution and changing the proportions of functional groups. With this objective, a complete upgrading study of chlorinated plastic pyrolysis oils was carried out comparing thermal and catalytic cracking. This research work attempts to provide a step forward towards the utilization of plastic pyrolysis oils as valuable fuels and/or chemical feedstock for refineries.

2. Material and methods

2.1. Pyrolysis oil samples and catalyst

The pyrolysis oils used for the experiments were two samples obtained by the authors in previous experiments of pyrolysis of municipal plastic waste, carried out in an installation consisting on a 3.5 L semi-batch reactor and a condensing system equipped with three condensers and an activated carbon column, and purged with a 1 L min⁻¹ N₂ flow [6,18]. More specifically, two pyrolysis oils samples have been used; (1) pyrolysis oils coming from several thermal pyrolysis of a mixture of 40 wt.% PE/35 wt.% PP/18 wt.% PS/4 wt.% PET/3 wt.% PVC carried out at 500 °C, atmospheric pressure, and dwell times from 0 to 120 min, and (2) pyrolysis oils coming from catalytic pyrolysis runs of the same

sample carried out with ZSM-5 zeolite at several different temperatures in the range 425–460 °C, atmospheric pressure, and dwell times of 30 min. These samples are called in this paper pyrolysis oil 1 (PO1) and pyrolysis oil 2 (PO2) respectively.

Pyrolysis oils obtained at different temperatures (PO1 at 500 °C and PO2 at 425–460 °C) were chosen because PO1 was obtained in thermal pyrolysis experiments and PO2 in catalytic pyrolysis experiments. In the installation used for the production of such oils, the optimum temperature (the temperature that produces the highest quantity of pyrolysis oils with the best properties) of the thermal pyrolysis is 500 °C. On the contrary, when a cracking catalyst is used, 500 °C is a too high temperature and 425–475 °C are more adequate ones. Therefore, the objective of such selection was to work with pyrolysis oil samples obtained at the best experimental conditions of the installation used for their production. The characteristics of both samples are shown and discussed in Section 3.

Waste Red Mud was used as catalyst for the experiments. Red Mud is a by-product of the alumina production process (Bayer process) composed mainly of Fe₂O₃. It has been proved by the authors in previous pyrolysis experiments that this product has a noticeable catalytic effect [17,18]; therefore, it is worthwhile further investigating its behavior as catalyst, given that it is an abundant and inexpensive industrial waste product. The composition and main characteristics of Red Mud are summarized in Table 1. More detailed information on its properties and characterization has been published elsewhere [18].

2.2. Upgrading pilot plant

The upgrading experiments were carried out in a lab-scale installation equipped with a stirred autoclave and a condensation system cooled by a coolant circulating liquid. Fig. 1 shows the flow-sheet of the upgrading pilot plant. In each experiment, 100 g of sample were placed in the autoclave, which was then closed, heated up to 325 °C at a rate of 5 °C min⁻¹, and maintained at such temperature for a 30 min dwell time. The installation was used in batch operation (closed autoclave) in order to maximize chemical reactions, thus the experiments were carried out at the auto-generated pressure (60–100 bar). Immediately after the dwell time finished, the opening valve of the autoclave was opened in order to let the formed volatile products flow to the condensation system, where the condensable vapors were condensed into light oil; the non-condensable gases were collected in plastic bags. The yields of light oil and of the heavy fraction remaining in the autoclave were calculated as weight percentage with respect to the amount of sample introduced at the beginning of the experiment. Gas yields were calculated by difference. In the catalytic runs, 10 g of Red Mud were mixed with the pyrolysis oils at the onset of the experiment; the catalyst remained in the autoclave after the experiment mixed with the heavy fraction.

2.3. Analysis of the products

The composition of the initial samples (pyrolysis oils) as well as the liquid fractions obtained after the cracking experiments (light fraction and heavy fraction) was determined by gas-chromatography coupled

Table 1
Main characteristics of red mud.

Composition (wt.%)	Fe ₂ O ₃	36.5
	Al ₂ O ₃	23.8
	TiO ₂	13.5
	SiO ₂	8.5
	CaO	5.3
	Na ₂ O	1.8
	Others ^a	10.6
BET surface area (m ² g ⁻¹)		27.5
Acidity (mmol NH ₃ g ⁻¹)		0.09

^a By difference.

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