LIQUEFACTION OPTIMIZATION OF CRATAEGUS MONOGYNA JACQ

[1]YULIYA DULYANSKA, [2]LUÍSA CRUZ-LOPES, [3]BRUNO ESTEVES, [4]IDALINA DOMINGOS,
[5]JOSÉ FERREIRA, [6]RAQUEL P. F. GUINÉ, [7]FERNANDO J. GONÇALVES,
[8]LUÍS BATISTA DE CARVALHO, [9]MARIA JOÃO BARROCA

[1,2,3,4,5,6,7]CERNAS, Research Centre, Polytechnic Institute of Viseu
[8,9]Molecular Physical-Chemistry R&D Unit, Department of Chemistry, University of Coimbra
E-mail: [1]ydulyanska@esav.ipv.pt, [2]lvalente@estgv.ipv.pt, [3]bruno@estgv.ipv.pt, [4]ijd@estgv.ipv.pt, [5]jvf@estgv.ipv.pt,
[6]raquelguine@esav.ipv.pt, [7]fgoncalves@esav.ipv.pt, [8]labc@ci.uc.pt, mjbarroca@esac.pt

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Abstract - The objective of this work was to evaluate the potentiality of Crataegus monogyna Jacq. residues to be liquefied by polyhydric alcohols and the chemical transformations observed in this process with subsequent use to produce polyurethane foams. The variations on liquefaction yield were determined at different temperature, time, material/solvent ratio and granulometry.

Results show that liquefaction performed at 180 °C with a 1:10 material/solvent ratio increases along time, reaching a maximum at 60 min. Similarly, liquefactions made during 60 min with a 1:10 material/solvent ratio show that there is an increase in liquefaction yield with the increase in temperature until 180 °C. A higher temperature could increase the liquefaction yield but would lead to a higher energy consumption in the process. There seems to be no significative advantage in increasing material/solvent ratio above 1:7, although the liquefaction yield increases for higher ratios. Granulometry testing shows that the smaller the particle the best is the liquefaction percentage. It was concluded that the best liquefaction yield, of approximately 81%, was obtained with a temperature of 180 °C, for 60 min and particle size <80 mesh for Crataegus monogyna Jacq. This material has good properties to be converted in a liquid mixture that can be used later, on the production of polyurethane foams.

Keywords - Crataegus monogyna; Liquefaction; Ecovalorisation; Residues.

I. INTRODUCTION

Crataegus monogyna, commonly known as hawthorn or single-seeded hawthorn, is a deciduous shrub or small tree belonging to the Rosaceae family [1]. Widely distributed across Europe, North Africa, and Western Asia, this species is celebrated for its ornamental value and has a rich history of traditional medicinal uses [2]. With its distinctive lobed leaves, fragrant blossoms, and vibrant red berries, Crataegus monogyna has not only adorned landscapes but has also captured the attention of researchers and herbalists due to its potential health benefits [3].

The medicinal properties of Crataegus monogyna have been recognized for centuries, with historical applications ranging from cardiovascular support to digestive remedies [3]. The plant is characterized by its content of bioactive compounds, including flavonoids, oligomeric proanthocyanidins, and triterpenoids, which contribute to its therapeutic potential [4]. As researchers delve into the biochemical composition and pharmacological effects of Crataegus monogyna, there is a growing interest in exploring its applications in modern medicine and nutraceuticals.

One of the most interesting facts associated with the application of biomass residues is that they can provide raw materials available to produce other products that generally are obtained from more hazardous sources and/or processes [5], [6]. In this way, the valorisation of the lignocellulosic biomass coming from pruning, such as the branches of the plants can improve sustainability while also having an economic impact. These materials constitute a low-cost raw material which may undergo chemical transformation to produce some biopolyol intermediates suitable to be applied as bio-based precursors to synthesize innovative polyurethane foams[7].

Polyhydric alcohols, such as glycerol and ethylene glycol, play a pivotal role in the field of chemical processing, particularly in the liquefaction process. Liquefaction involves the conversion of solid biomass materials into a liquid form, offering a versatile approach to produce bio-based chemicals. Several studies were made that prove the efficiency of polyhydric alcohols liquefaction as for example the optimization of liquefaction processes using mixtures of glycerol, polyethylene glycol, and KOH for Douglas-fir bark [8] or the liquefaction of chestnut shells [9]. The findings contribute to a comprehensive understanding of the liquefaction process, guiding sustainable applications for chestnut-derived feedstocks. Furthermore, Fernandes et al. [10] extended the exploration to Eucalyptus globulus bark and branches, showcasing the eco-valorization potential through liquefaction.

The focus on polyhydric alcohols in this context is driven by their unique chemical properties, making them promising candidates for diverse applications, including the synthesis of polyurethane foams.

Polyurethane foams are widely utilized in various industries due to their exceptional insulation properties, lightweight nature, and versatility. The liquefaction of polyhydric alcohols provides a sustainable pathway to produce feedstocks that can be employed in the synthesis of polyurethane foams.

This process aligns with the growing global emphasis on developing eco-friendly alternatives to traditional petrochemical-based materials. There are several publications on the production of polyurethane foams from liquefied lignocellulosic materials utilizing unconventional sources such as orange-peel wastes [11], Eucalyptus globulus branches [10] and chestnut shells [9].

As referred, the liquefaction of polyhydric alcohols holds significant relevance in the production of polyurethane foams. By exploring into the details of the liquefaction process, its conditions, and the resulting products, we aim to shed light on the sustainable and innovative use of polyhydric alcohols in the synthesis of polyurethane foams, contributing to the ongoing efforts toward a more environmentally conscious and resource-efficient future.

In this scope, the potential of Crataegus monogyna Jacq. residues to be liquefied by polyhydric alcohols was evaluated.

This sets the stage for further exploration into the botanical, ecological, and medicinal aspects of Crataegus monogyna, highlighting its significance as a plant of cultural, aesthetic, and potential therapeutic importance.

II. MATERIALS AND METHODS

The methodology involved the preparation of Crataegus monogyna branches by air-drying at room temperature, followed by crushing using a Retsh SKI mill (Retsch GmbH, Haan, Germany) and subsequent sieving with a Retsch AS200 at 50 rpm for 30 minutes. The resulting fractions, namely > 40 mesh (0.450 mm), 40-60 mesh (0.425-0.250 mm), 60-80 mesh (0.250-0.180 mm), and < 80 mesh (< 0.180 mm), were used for subsequent tests. Prior to testing, these fractions were dried in a greenhouse at 100 °C for 24 hours (Figure 1). Analytical grade reagents were employed for the experiments.

To explore the optimal liquefaction conditions for Crataegus monogyna branches, various parameters including reaction times, temperature, and sample sizes were investigated. The liquefaction process was executed in a double-shirt reactor (600 mL) heated with oil (Reactor Parr LKT PED). Branch samples were introduced into the reactor along with a 1:1 mixture of glycerol and ethylene glycol, catalysed with 3% sulfuric acid. The liquefied samples were subsequently dissolved in methanol and filtered.

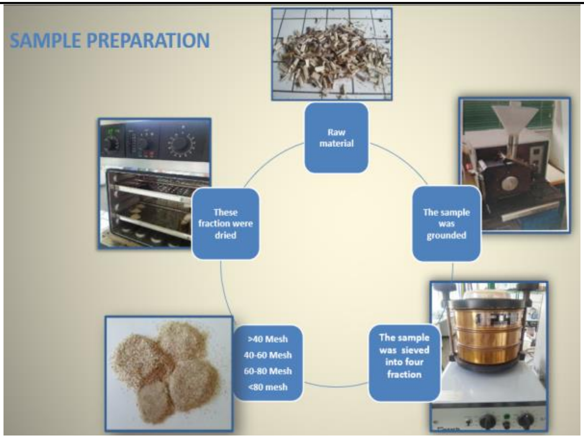

Figure 1. Sample preparation

The influence of particle size was examined across the five fractions. The temperature range for liquefaction varied between 140 °C and 180 °C, and liquefaction times spanned from 15 to 60 minutes, with a specific focus on the 60-minute mark. Additionally, different ratios of Crataegus monogyna to solvent (CM:solvent) were assessed, specifically at 1:3, 1:5, 1:7, and 1:10. This comprehensive approach aimed to unravel the intricate interplay of various factors in optimizing the liquefaction process for Crataegus monogyna branches.

III. RESULTS AND DISCUSSION

The experimental results presented on Figure 2 demonstrate that the liquefaction process, conducted at a temperature of 180 °C with a material/solvent ratio of 1:10, exhibits an increase in yield over the course of 60 minutes, eventually reaching a peak.

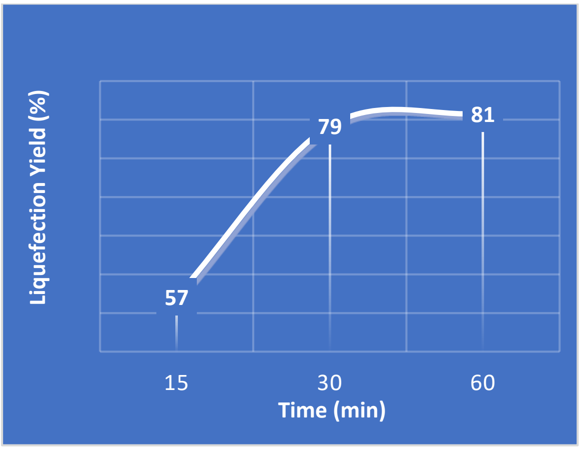

Figure 2. Liquefaction yield variation with time. Tests conducted at 180 °C

It is noteworthy that pushing temperatures beyond this point could potentially enhance liquefaction yield but would come at the cost of increased energy consumption during the process. Therefore, higher liquefaction time was not tested since it is economically useless to take more than one hour in the process.

Liquefactions conducted over a 60-minute period, utilizing a material-to-solvent ratio of 1:10, indicate a visible rise in liquefaction yield as the temperature increases, reaching its peak at 180 °C (Figure 3). This observation emphasizes the positive correlation between temperature increase and the efficiency of the liquefaction process, suggesting that higher temperatures contribute to enhanced liquefaction yields within the specified temperature range.

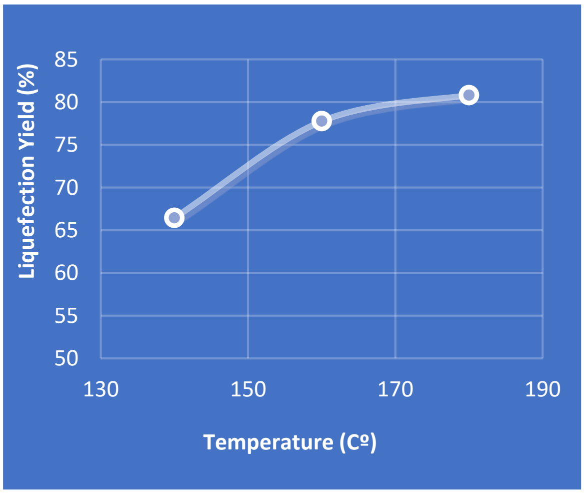

Figure 3. Liquefaction yield variation with temperature. Tests conducted for 60 min

Interestingly, granulometry testing (Figure 4) reveals a correlation between particle size and liquefaction percentage. The smaller the particle size, the more pronounced the liquefaction, emphasizing the importance of particle size in optimizing the liquefaction process.

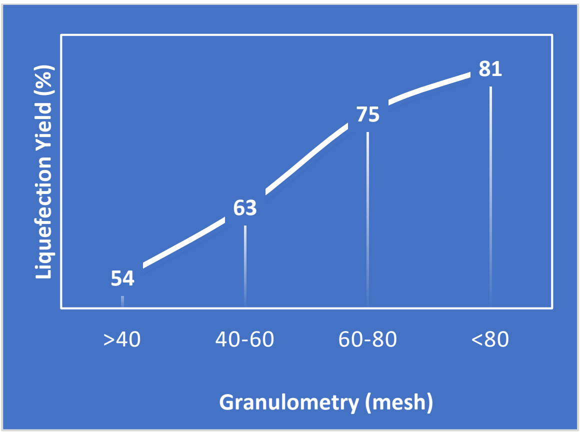

Figure 4. Liquefaction yield variation with granulometry. Tests conducted at 180 °C during 60 min

Concerning the material/solvent ratio (Figure 5), higher amounts of solvent lead to higher liquefaction yields, however there is no advantage in exceeding a ratio of 1:10. Despite this, liquefaction yields continue to increase for higher ratios, indicating a nuanced relationship between material/solvent proportion and liquefaction efficiency.

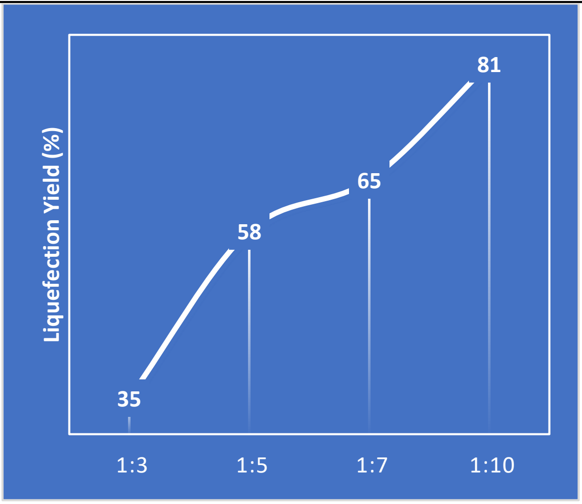

Figure 5. Liquefaction yield variation with material/solvent ratio. Tests conducted at 180ºC during 60 min

IV. CONCLUSIONS

Summarizing the optimal conditions for Crataegus monogyna Jacq.: the highest liquefaction yield, approximately 81%, is achieved at a temperature of 180 °C for 60 minutes, with a particle size of less than 80 mesh.

This suggests that the material holds favourable properties for conversion into a liquid mixture, positioning it as a promising candidate for subsequent use in the production of polyurethane foams. These findings provide valuable insights into the intricate interplay of temperature, duration, material/solvent ratio, and particle size in optimizing liquefaction processes for potential industrial applications.

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