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DESIGN OF A BATCH SOLVOLYTIC LIQUEFACTION REACTOR FOR THE VALORIZATION OF RESIDUES FROM THE AGRICULTURAL FOODSTUFF

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Olive stone residues (23%wt) were liquefied in phenol (71%wt) in the presence of sulfuric acid (6%wt) as catalyst at 170°C during 2 h. A 500 ml classic reactor under atmospheric conditions was used to establish the characteristics of the new 2001 liquefaction reactor. The liquefied products can be used as raw material for phenol-formaldehyde resins. The batch feeding procedure, the average temperature and the configuration of the reactor largely determined the viscosity and the molecular weight of the liquefied products. These parameters were positively modified by the constantly presence of olive stone moisture and water from depolymerization in the reaction medium. A jacketed cooling wall in the upper half of the 2001 reactor and a heat exchanger were necessary to accelerate vapour condensation, and to improve the contact in the reaction mixture. The recovery of liquefied products was also improved by using a closed container with a pressure-equalizing system that avoids the release of phenol vapour to the atmosphere.

Keywords: olive stones; water; cellulose; feedstock procedure; liquefaction reactor.

INTRODUCTION

The declining availability of landfill and the increasing amounts of biomass waste cause environmental pollution. Nowadays, the olive industry represents a major activity in Southern Europe and the Mediterranean basin, which produces 2.4 Mt of oil per year (95% of the world production) and revenue for 2 million enterprises. The olive produces 20% of oil and 80% of solid/liquid residue. The latter amounts to 30 Mt per year, much more than the actual production of oil. The final solid residue, *orujillo*, is produced basically by the pomace oil (*aceite de orujo*) industry. The olive stones have high lignin, cellulose and hemicellulose contents and represent an important local source of lignocellulosic materials. Potential sites in lignocellulosics materials are secondary hydroxyls, carbonyls, carboxyl (ester), carbon-carbon, ether and acetal linkages. More recently, many attempts have been made to liquefy wood in the presence of solvents: phenol, bisphenol A, benzyl alcohol and oxyethers with acidic catalyst at moderate temperature and without catalyst at elevated temperatures to produce phenol-formaldehyde-type resins (Lin *et al.*, 1995; Maldas *et al.*, 1997). In the same manner, the olive stones naturally containing biopolymer can be analogously transformed by liquefaction into new polymer materials. The optimized liquefaction conditions showed that 23%wt of olive stone can be completely liquefied in 70%wt of phenol and 6%wt of sulphuric acid. Specifically, phenol-formaldehyde type mouldings from the liquefied

olive stones have been prepared. The liquefied olive stones replaced about 70% of phenol used during resin cooking. The physical and mechanical properties of the biopolymers obtained were comparable to its corresponding commercial products. In order to produce the raw material (liquefied products) for biopolymer fabrication, the liquefaction of the olive stones needs to be carried out in a reactor which satisfies both the liquefaction and further polymerization restrictions. The present paper will focus on the process development and design aspects of the liquefaction reactor.

EXPERIMENTAL

Equipment

A liquid/solid catalysed reaction mixture was used to assess the performance of the olive stones liquefaction stirred reactors. A 500 ml classic reactor was heated with an oil bath system, and was equipped with a mechanical stirrer, and three feedthrough sealed necks to accommodate a thermocouple, a reflux condenser and the reagents inlet.

Raw Materials

Olive stones from Spain without pulp were used for liquefaction at different particles sizes. Analysis of undried olive stones revealed 10% water, 6% lignin, 24% hemicelluloses, 59% cellulose and small amounts of extractives. Phenol 99% was used as liquefying reagent and sulphuric

acid 98% as catalyst. Dried olive stones were prepared in an oven at 103°C for 24 h and kept in a desiccator at room temperature before use.

Measurement

Residue content

The liquefaction product was diluted in acetone and filtered through a Toyo GA 100 glass filter to separate liquid from solid products. The solid residue was methanol-extracted in a Soxhlet apparatus during 24 h. The solid was dried in an oven at 103°C for 24 h. The residue content is defined as the percentage dry weight ratio of the solvent insoluble substances to the total lignocellulosics charged into the reactor. It is usually used as an index of the liquefaction yield.

Viscosity

Rheovisco RIM equipment was used to determine the viscosity of the liquefaction product at room temperature under the following conditions: rotor number 5, speed 30 rpm.

Gel permeation chromatography

The molecular weight of the soluble fraction of the liquefied product was determined on a Shimadzu GPC system comprised of LC-9A pump, refractive index detector model RID-6A and two columns connected in series: a Plgel 5 μm , 500 \AA , 300 \times 7.5 mm column and a Plgel 5 μm , 100 \AA , 300 \times 7.5 mm column. A 100 μl sample was injected into the eluent flow. Owing to the complexity of the products, a solution of lithium chloride in dimethyl formamide was selected and successfully used as eluent (DMF-LiCl 0.1 M). The samples were eluted isocratically (1 ml min⁻¹). Each analysis lasted 30–35 min. The molecular weight was calculated based on PEG standards.

RESULTS AND DISCUSSION

Liquefaction and Feeding Procedure

Liquefaction was carried out using phenol (71%wt), olive stones (23%wt) and sulphuric acid as catalyst (6%wt). The oil bath was kept at 170°C and the time of liquefaction, timed after the addition of catalyst, was fixed to 120 min.

The feeding procedure is a basic parameter to be considered in the liquefaction of biomass. Three different procedures were studied that led to different reaction temperatures inside the reactor.

Procedure 1

The reagents and biomass were added at the same time. The reaction was conducted during 120 min.

Procedure 2

Only the biomass and the phenol were introduced into the heated reactor. After 60 min, the temperature inside the reactor levelled off at 160°C, then the catalyst was added and the reaction was performed during 120 min.

Procedure 3

Phenol was introduced into the heated reactor. When phenol reached 170°C, the biomass was added and 100 min later, the catalyst was also added. After 120 min the reaction was stopped.

Table 1 shows the principal characteristics of the liquefied product as raw material for polymer production: the viscosity and the final residue content (RC) obtained with different feeding procedures.

From each procedure, the average temperature was determined to study the liquefaction as well as the feasibility process of using the liquefied products as raw material in the PF resins system. It was observed that viscosities higher than 150 Poises led to important modifications to the traditional PF resins process, and that residue contents higher than 2% can modify the physical and mechanical characteristics of the final biopolymer. It was also observed that the temperature inside the reactor during liquefaction depended largely on the feeding procedure. Moreover, the temperature had a direct effect on the mentioned parameters: the higher the final average temperature, the higher the viscosity and the lower the residue content.

Procedures 1, 2 and 3 are represented by Figure 1 (a–c). This figure shows the trend of the temperature during the reaction and indicates the final average temperature value observed. The reaction never reaches the oil bath temperature (170°C) in any case. However before the addition of catalyst, the phenol and the biomass can reach such a temperature (as in the first minutes of procedure 3). Therefore, a better performing heating system was used to diminish the cooling phenomenon during liquefaction and to reach the desired temperature. The feeding procedure 1, which showed the lowest average temperature (125°C), was used to assess the experience. As a result the average temperature observed this time was about 150°C. Surprisingly, the viscosity of the liquefied product increased also by more than 200 Poises under these conditions, that is, more than in procedure 3, which also showed the same high average temperature and non-desirable characteristics of liquefied products. These findings suggest that high temperatures inside the reactor generated by the implementation of feeding procedures 2 or 3 or by any external mechanical means produce an important modification of the reaction as well as in the liquefied products. Anyway, a decrease in the temperature was always observed in all the cases after addition of the catalyst, which confirms the beginning of the reaction.

These results can be ascribed to the presence of water vapors in the early stage of liquefaction, produced during the reaction and the water released from the moisture olive stones. Water cools down the medium and further

Table 1. Influence of the FP procedure on the characteristics of liquefaction products.

| Feedstock procedure | RC, %wt | Viscosity, Poise | Average temperature T_{IR} , °C | PF resins feasibility |
|---------------------|---------------|------------------|-----------------------------------|-----------------------|
| Procedure 1 | 1.7 \pm 0.2 | 90 | 125 | Feasible |
| Procedure 2 | 1.7 \pm 0.2 | 150 | 138 | Unfeasible |
| Procedure 3 | 0.1 \pm 0.2 | 209 | 149 | Unfeasible |

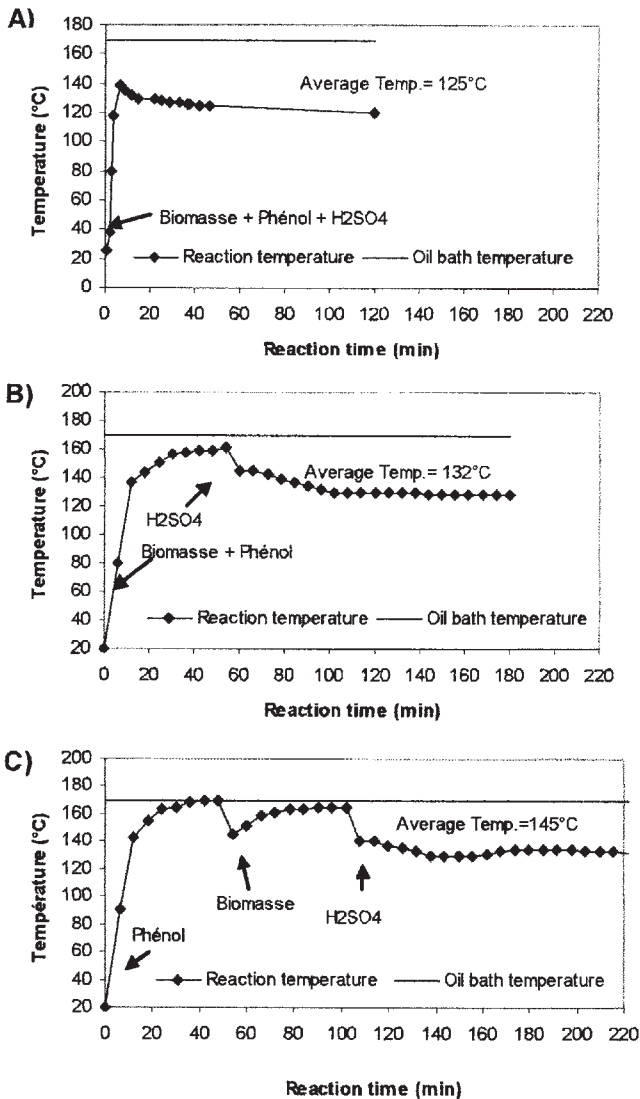


Figure 1. Temperature profiles of olive stones liquefaction with phenol (71%) and sulphuric acid (6%) according to: (A) procedure 1; (B) procedure 2; (C) procedure 3.

participates in the reaction, modifying the physical characteristics of the liquefied products.

Influence of Water During the Liquefaction

It was confirmed that water can play a determinant role during the liquefaction reaction (Lin *et al.*, 2001; Pizzi and Stephanou 1994; Pu and Shiraishi 1993), especially in the cellulose hydrolysis and its recondensation (Yamada *et al.*, 1996, 2002; Tejada-Ricardez *et al.*, 2002). Water in the reaction medium can come from two sources: the moisture naturally contained in the olive stones, and the water produced during the lignin degradation mechanism, as described by Lin *et al.* (2001). It was demonstrated that guaiacyl guaiacol ether, a model compound of lignin, reacts with phenol during liquefaction in acidic medium to produce, among other compounds, formaldehyde. The latter can condense with phenol to yield diphenylmethane compounds and water. It was observed that cellulose recondenses and produces insoluble substances under specific

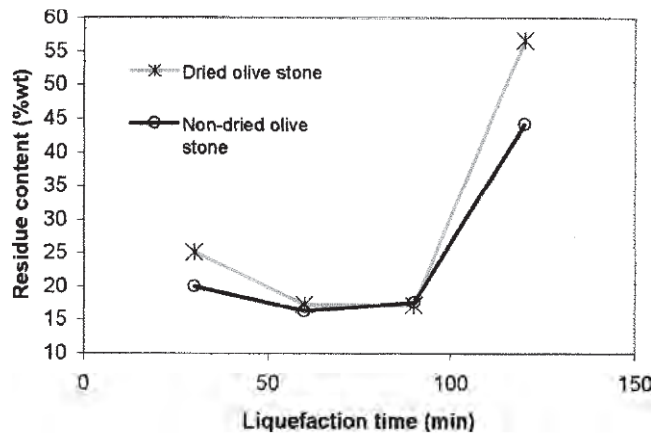


Figure 2. Residue content after liquefaction of dried and non-dried olive stone at different liquefaction time.

liquefaction conditions. Figure 2 shows the influence of water during the liquefaction of olive stones under previously studied liquefaction conditions (Tejada-Ricardez *et al.*, 2002). The residue content was used to assess this phenomenon.

Large amounts of dried and undried olive stones were liquefied with low phenol quantities to favor the recondensation conditions and to study the importance of water during the liquefaction. It was observed under these conditions that a high concentration of insoluble substances was produced during the liquefaction of dried olive stones. When water was present, a decrease in the residue content was observed during the liquefaction of un-dried olive stones under similar conditions. These results confirm the importance of improving the contact between the water released and the water produced during the liquefaction with the reaction medium. The absence of water in the medium, after the increase in the average temperature in the reactor by any means, produces important modifications in the final liquefaction product. We decided thus to conceive an improved batch liquefaction reactor (ILR) taking into account the previous restrictions and necessities of a system for the liquefaction of lignocellulosics wastes. Our main objective was to establish a compromise between liquefaction restrictions (low residue contents) and the following polymerization requirements procedure (PF resins system).

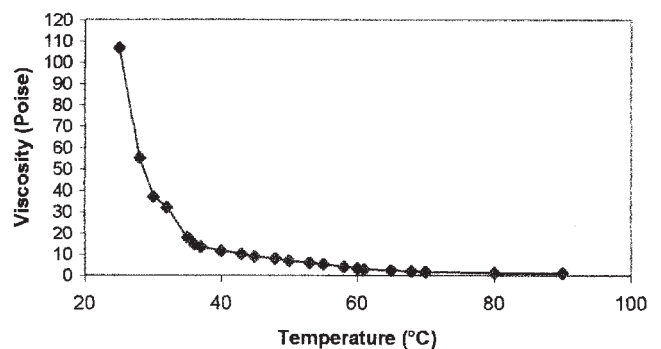


Figure 3. Viscosity of the liquefied product at different temperatures.

New Reactor Design

After reaction, the liquefied product is recovered and analysed to prepare the biopolymer. Figure 3 shows that the viscosity increases drastically when cooling after reaction and reaches more than 100 Poise at room temperature. The high viscosity of the liquefied product can produce loss of material during the recovery as it adheres to the wall. By using methanol as diluting solvent, the liquefaction products can be totally recovered. However, the use of an organic solvent increases the cost of the process and requires the addition of a second step for solvent recycling.

Another solution is the recovery of the products at high temperature. This alternative requires adaption of an outlet valve at the bottom of the reactor connected to a closed container since the liquefied product releases phenol vapour at high temperatures. Figure 4 shows the scheme of the improved liquefaction reactor that uses a recovery container adapted with a pressure-equalizer system.

Another feature is the heated container A for the feeding of phenol, which melts at 43°C. The feeding containers supply the reactive and raw material to the reactor according to the feeding procedure 1. The valve above container A

allows phenol to flow to the reactor. Container B stocks the olive stones which flow in a second step, and finally the liquid catalyst, contained in the container C, is added to start the reaction. The reaction is carried out at 170°C during 120 min.

However, the main characteristic of this reactor is a cooling jacketed wall in the upper half of the reactor. By this means the contact of the condensed water with the liquefaction products during the reaction is improved. The double wall maintains the temperature of the upper half of the reactor far below than in the lower half. Its function is to accelerate the vapour condensation using a flow of cooling water. Water condenses directly on the wall of the reactor, very close to the reaction medium, and falls down directly into it. Vapour that cannot condense on the cold wall of the reactor will be condensed in the external heat exchanger and recycled to the reaction medium through a central reflux system, assuring a constant flow of water.

Table 2 shows four reaction conditions that were used to validate the design of the improved reactor. Results are shown in Table 3, which clearly demonstrate the advantage of the improved liquefaction reactor (ILR) against a traditional reflux reactor (TRR).

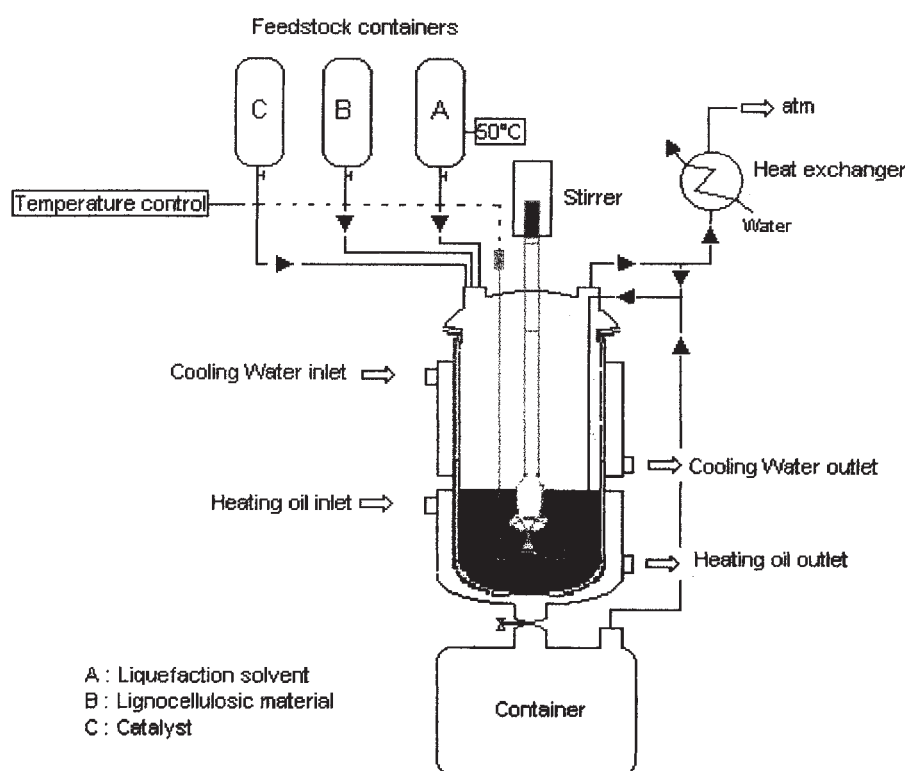


Figure 4. Improved liquefaction batch reactor.

Table 2. Conditions for the liquefaction of olive stones using a TRR and the ILR. Feeding procedure 1.

| Experiment no | Time, min | Catalyst, %wt | Phenol, %wt | Biomass, %wt | Particle size, μm | Temperature, $^{\circ}\text{C}$ |
|---------------|-----------|---------------|-------------|--------------|------------------------------|---------------------------------|
| Reference | 120 | 6 | 73 | 23 | 920 | 170 |
| 1 | 68 | 7 | 66 | 27 | 920 | 170 |
| 2 | 103 | 7 | 66 | 27 | 920 | 170 |
| 3 | 103 | 3 | 61 | 36 | 920 | 170 |
| 4 | 85 | 4 | 70 | 27 | 1616 | 170 |

Table 3. Residue content, viscosity and molecular weight of the liquefied product obtained in TRR and IRL.

| Reactor-number experiment | RC, %wt | Viscosity, Poise | M _w Da |
|---------------------------|------------|-------------------|-------------------|
| Reference | 1.1 ± 0.2 | 126 | 1649 |
| ILR-1 | 2.9 ± 0.2 | 150 | 1978 |
| TRR-1 | 2.6 ± 0.2 | Practically solid | 2615 |
| ILR-2 | 4.4 ± 0.5 | 215 | 1664 |
| TRR-2 | 1.0 ± 0.3 | 848 | 2020 |
| ILR-3 | 16.6 ± 0.2 | 4550 | 1625 |
| TRR-3 | 18.6 ± 0.3 | Practically solid | 2309 |
| ILR-4 | 7.2 ± 0.2 | 320 | 1700 |
| TRR-4 | 0.7 ± 0.2 | Practically solid | 2100 |

A decrease was observed in the viscosity and molecular weight when using the improved reactor. Most of the liquefaction conditions led to low residue content with both reactors. However, only the liquefaction products obtained with the ILR were appropriate as raw material for PF resin production.

Moreover, the experience labelled as Reference in Table 3 was obtained under optimized conditions in the optimized reactor. It was successfully used to replace about 70%wt of the phenol used in the PF resin system.

CONCLUSION

It was observed that the feeding procedure largely determined the physical characteristics of the liquefied products. Among the three different feeding procedures studied, the procedure that added all the reagents at the beginning of the reaction led to the lowest average temperature during liquefaction and to the best characteristics of the liquefaction products. It was demonstrated that the average temperature during liquefaction also plays an important role in the viscosity, the residue content and the molecular weight of the product. The feeding procedure and the design of the reactor can modify such temperature. Results suggest that water is associated with this phenomenon. The water released from the raw material and the water produced during the degradation diminishes the viscosity and the molecular weight of the liquefaction product only if the reactor design allows water to be significantly in contact with the reaction medium. A jacketed cooling wall was installed in the upper half section of the reactor to improve and accelerate the vapour condensation in the neighbour-

hood of the reaction medium. A second double wall containing hot oil serves to provide the heat to start and maintain the reaction. Finally, a closed container with a pressure-equalizer system allows the recovering of the liquefaction product at hot temperatures to diminish the loss by increase in the viscosity and by phenol evaporation. All these features improve the design for the batch liquefaction reactor, but with higher energy consumption which is necessary for the quality and improved yield of the liquefaction product.

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ADDRESS

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