

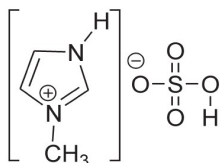
Valorization of waste cooking oils through [HMIM][HSO₄] ionic liquid-catalyzed biodiesel conversion

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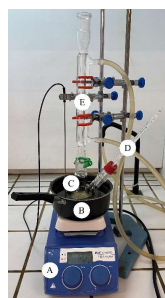
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INTRODUCTION & AIM

A recent trend is the search for alternative technologies to fossil fuel-based energy sources. One possible solution is to use biodiesel as a diesel substitute, reducing environmental impacts such as pollutant emissions. Biodiesel consists of a mixture of long-chain fatty acid alkyl esters and is produced by converting vegetable oils or animal fats by transesterification reactions (Ullah *et al.*, 2015). Due to the relatively high raw material cost, there is a need to reduce the final price of biodiesel. Thus, oil sources not competing with the food market, such as waste cooking oils (WCOs), are used. However, these oils show high levels of free fatty acids (FFA), which can cause problems in alkaline transesterification in the classic biodiesel production process. To minimize these problems, ionic liquids (ILs) can be used as catalysts, since they also promote esterification reactions of FFA to biodiesel. ILs present a few advantages related to their recoverability and reusability, as well as environmental and safety perspectives (Ullah, 2015). Thus, the objective of this work is to study the production of biodiesel by applying 1-methylimidazolium hydrogen sulphate IL ([HMIM][HSO₄]) (see Fig. 1) as a catalyst in esterification/transesterification reactions with methanol, for oleic acid (OA) and samples of simulated high acidic oils, prepared by a mixture of 40%(w/w) OA and 60%(w/w) WCO. The IL recovery procedure was studied to evaluate the maximum number of recovery cycles that can be performed without significant loss of reaction yield.

Figure 1. IL [HMIM][HSO₄] chemical structure

METHOD



• Biodiesel production

A – heating plate with automatic temperature control and magnetic stirring, B – paraffin bath, C – reactor, D – thermometer, E – reflux condenser

A – heavy phase (glycerol)
B – light phase (biodiesel)

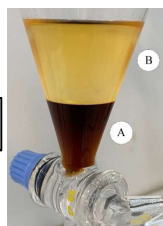


Figure 3. Phase separation

Figure 2. Biodiesel production experimental apparatus

• Conversion assessment

- **Acidity value** (AV) determined according to a procedure based on the European Standard EN 14104/2003.
- Reaction conversions assessed through AV drop.

$$AV \left(\frac{\text{mgKOH}}{\text{g sample}} \right) = \frac{V_{\text{KOH}} \times C_{\text{KOH}} \times MM_{\text{KOH}}}{m_{\text{sample}}}$$
$$X (\%) = \frac{AV_{\text{initial}} - AV_{\text{final}}}{AV_{\text{initial}}} \times 100$$

- **Biodiesel FAMES content** determined by GC-FID, through a procedure in accordance with the European Standard EN 14103/2003, using methyl heptadecanoate as internal standard (IS).
- Reaction conversions assessed through FAMES content.

$$X (\%) = \frac{(\sum A_{\text{FAMES}} - A_{\text{IS}})}{A_{\text{IS}}} \times \frac{C_{\text{IS}} \times V_{\text{IS}}}{m_{\text{sample}}} \times 100$$

• Catalyst recovery and reuse study

- **IL recovery** carried out by washing the glycerol phase with distilled water, on a 1:3 sample/solvent mass ratio.
- Heavy phase dried, reused, and analysed by FTIR after the final cycle.



Figure 4. IL recovery

RESULTS & DISCUSSION

OA and a simulated high acidic oil (SHAO), prepared by a mixture of 40% (w/w) OA and 60% (w/w) WCO, were used as raw materials. The selected reaction conditions were: temperature of 65°C, reaction time of 4 hours, raw material/methanol molar ratio 1:10, and 10% (w/w) IL in relation to the raw material.

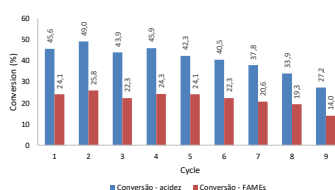


Figure 5. Conversion evolution (SHAO) for 9 reaction cycles (series 1)

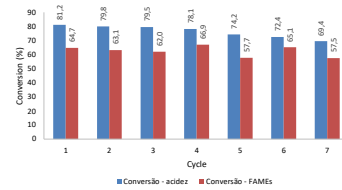


Figure 6. Conversion evolution (OA) for 7 reaction cycles (series 2)

Table 1. WCO treatment results for 4 reaction cycles (series 3)

Reaction	Reaction conditions	Treated oil AV (mg KOH/g)	Conversion AV drop (%)	FAME content (%)
3.1	65°C, 4h, 1:15, 15% w/w	1.8	71.3	5.1
3.2	65°C, 4h, 1:15, 10% w/w	2.4	61.5	3.5
3.3	65°C, 4h, 1:20, 10% w/w	1.9	67.9	3.3
3.4	65°C, 4h, 1:20, 15% w/w	1.9	68.1	3.3

- WCO AV – 6.1 mg KOH/g
- Low FAME content values – only FFA esterification occurred.
- Observed catalyst activity through four reaction cycles.

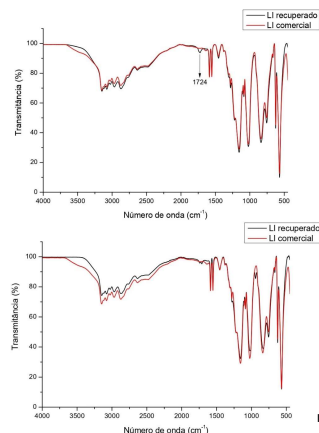


Figure 7. FTIR correlation for IL recovered in reaction cycle 2.7 – 99.3%

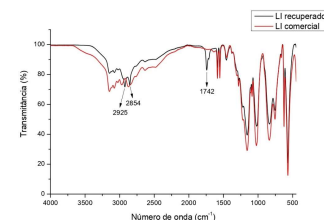


Figure 8. FTIR correlation for IL recovered in reaction cycle 1.9 – 90.0%

Figure 9. FTIR correlation for IL recovered in reaction cycle 3.4 – 97.6%

CONCLUSION

- Using OA, an initial conversion of 81.2% was obtained regarding acidity reduction.
- After seven reaction cycles, the conversion dropped to 69.4%, while the content of FAMES in the biodiesel produced decreased from 64.7% to 57.5%.
- Using SHAO, an initial conversion of 45.6% was obtained; after nine reaction cycles, the conversion decreased to 27.2%, while the FAMES content in the biodiesel decreased from 24.1% to 14.0%.
- Correlation between the FTIR spectra that relate final IL and initial commercial IL was 99.3% for OA and 90.0% for SHAO tests; the recovery method by water washing proved efficient.
- IL promotes only the esterification reaction.
- WCO treatment reactions allowed the reduction of its acidity to values between 1.8 and 2.4 mg KOH/g, and the FAMES content of the treated oil samples varied between 3% and 5%; no significant transesterification occurred under these conditions.

REFERENCES

Z. Ullah, M. A. Bustam, Z. Man, Renewable Energy, 77 (2015) 521-526.