CALCIUM RICH FOOD WASTES BASED CATALYSTS FOR BIODIESEL PRODUCTION

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Objective: Biodiesel (FAME) production using solid and liquid wastes from food industry in Portugal.
Biodiesel

First generation biodiesel (FAME) is pointed out as a feasible substitute of fossil diesel

Oil + methanol $\rightarrow$ FAME + Glycerin

- Non toxic
- Biodegradable
- RENEWABLE
- Better combustion with lower toxics emissions
Biodiesel can be produced from vegetable oils (edible or non edible), animal fats or even recycled greases from food industry, restaurants or domestic waste. In 2010 the amount of waste frying oils (WFO) manufactured in Portugal was 43,000 - 65,000 t.

Natural calcium sources from wastes can be used to prepare CaO catalyst for biodiesel production. In last year in Portugal were captured 749 t of crustacean, 19,172 t molluscs. Egg production for consumption 106,784 t.
Cheap raw materials like waste frying oils and animal fats will allow to reduces the biodiesel production costs.

**Drawbacks of low grade fats**
- high acidity
- high water content

Basic catalysts will be deactivated by neutralization and soap formation.

The use of mixtures of low grade fats with vegetable oil can overcome such drawbacks.
Experimental Procedure

Preparation of the catalysts

- Washing and drying at 120ºC of the as received shells
- Crushing and sieving
- Calcination in a muffle at 800ºC (3h)

The calcination temperature was selected from the thermal degradation profile of the raw shells obtained by thermogravimetry under air flow.

\[
\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2 \text{ for } T > 800^\circ \text{C under air}
\]
Transesterification and Catalyst Separation Process

Biodiesel reaction (100 g oil; 5 % w_{cat}/w_{oil}; methanol reflux temperature; molar racio methanol/oil=12; 2.5 h)

The catalyst separation from the reaction products

Reaction products with catalyst

Biodiesel

Glycerol
Biodiesel Purification Process

1. Decantation: Biodiesel is separated from the reactor, producing Glycerol and wash water.
2. Wash 1: Biodiesel is washed with water, producing wash water.
3. Acid Washing Solution: Biodiesel is treated with an acid washing solution, producing wash water and a washable solution.
4. Drying: Biodiesel is dried at >100°C for 30 minutes.
5. Centrifugation: Biodiesel is centrifuged at 4000 rpm for 5 minutes, producing waste.
6. Wash 3: Biodiesel is washed with water, producing wash water.
Results

Catalyst Characterization

Figure 1 - XRD patterns of fresh catalysts prepared by calcination at 800ºC.
Lime: CaO; Portlandite: Ca(OH)₂; Calcite: CaCO₃.

Figure 2 - Shows the DTA profiles of 9 raw Ca wastes as fresh catalysts.
**Biodiesel Characterization**

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**Figure 3** – FAME yield, assessed by thermogravimetry, obtained for soybean oil using the lime catalysts from Ca rich alimentary wastes (5 % \( w_{\text{cat}}/w_{\text{oil}} \); molar ratio methanol/oil=12; 2.5 h).

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**Table 1** – FAME yield using Waste Frying Oil (WFO) and WFO/Soybean (Soy) mixtures assessed by thermogravimetry (under air, 30 °C/min).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Raw-material</th>
<th>FAME yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scallop</td>
<td>50%WFO_50%Soy</td>
<td>90.9</td>
</tr>
<tr>
<td>Shellmix</td>
<td>75%WFO_25%Soy</td>
<td>82.0</td>
</tr>
<tr>
<td>Shellmix batch#1</td>
<td>WFO</td>
<td>62.5</td>
</tr>
<tr>
<td>Shellmix batch#2</td>
<td></td>
<td>88.4</td>
</tr>
</tbody>
</table>
Conclusions

✔ In standard conditions high FAME yields were obtained for all the tested catalyst with alimentary refined soybean oil.

✔ When used pure WFO a decline of the catalyst activity was observed, FAME yield decreased and was observed soap formation, this is due to WFO acidity be quite higher 2mg KOH/g oil.

✔ WFO can be processed mixed with neutral oil without significant loss of the catalytic performance.

✔ These natural catalysts are very active and suitable for biodiesel production through the transesterification process.
Future Work

✓ Optimization of reactions;

✓ Stability study of catalytic process;

✓ Study of the kinetics catalytic reaction;

✓ Study catalysts in nanostructured form.
Acknowledgement

We want to thank the FCT – Fundação para a Ciência e Tecnologia, Lisboa, Portugal, for funding project PTDC/EMS-ENE/4865/2014, to Instituto Superior Técnico (IST), Laboratory of Tecnology ADEQ and Centro de Estudos de Engenharia Química from ISEL, for laboratory and equipment utilization.
References


Thank You For Your Attention