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CALCIUM RICH FOOD WASTES BASED CATALYSTS FOR BIODIESEL PRODUCTION

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Contents

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

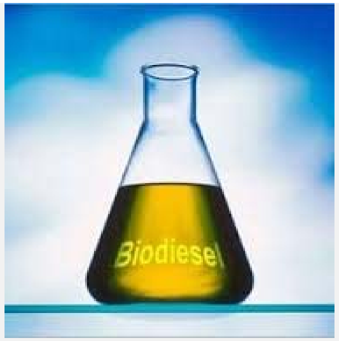
Waste Ca rich shells

WFO

CH3OH

FAME

Biodiesel



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

Oil + methanol → FAME + Glycerin

- Non toxic
- Biodegradable
- Better combustion with lower toxics emissions
- RENEWABLE

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.

Lard

Vegetable oil

WFO

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.

Raw materials

Cheap raw materials like waste frying oils and animal fats will allow to reduces the biodiesel production costs

Lard

WFO

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

Eggs and mollusk shells are Ca rich materials mainly $CaCO_3$

- 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

$$CaCO_3 \Rightarrow CaO + CO_2 \text{ for } T > 800^{o}C \text{ under air}$$

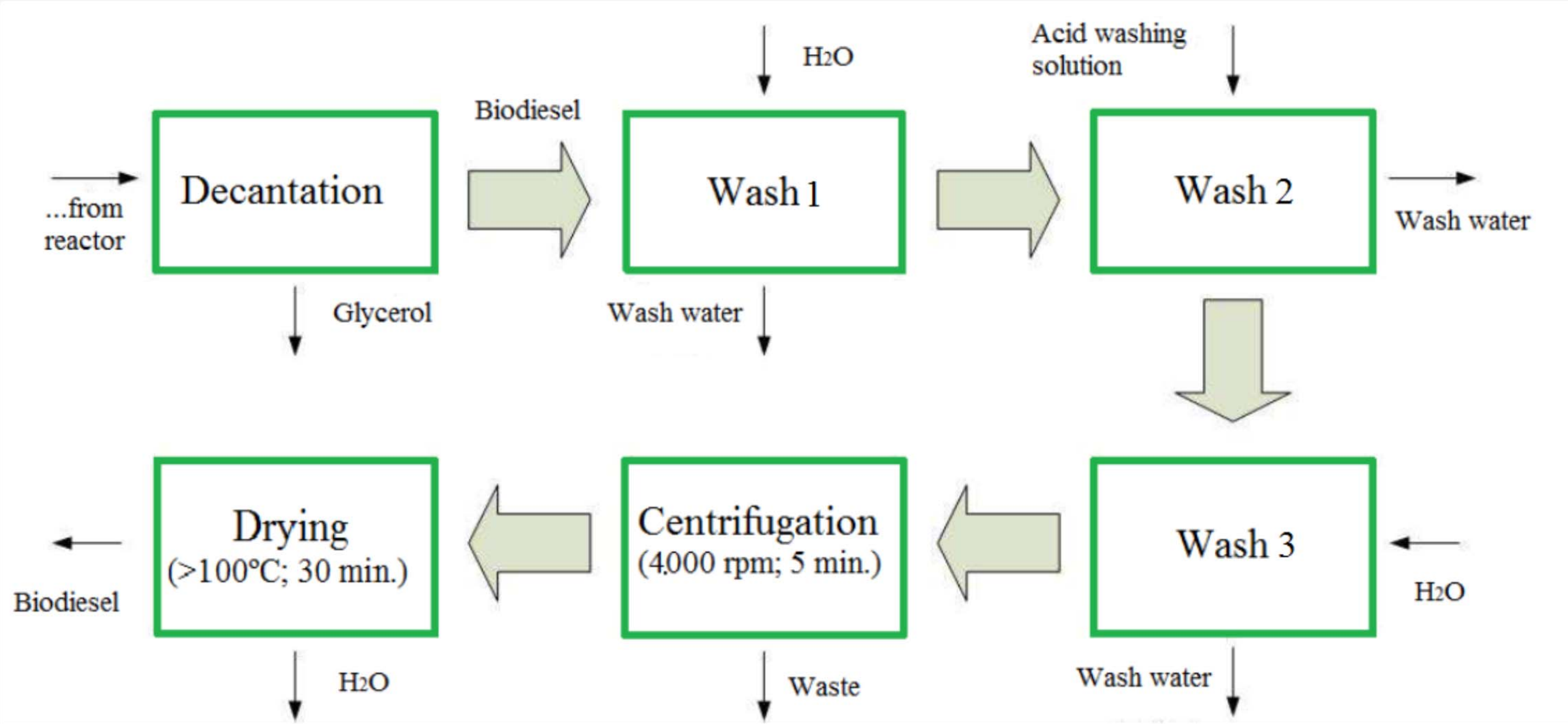
Transesterification and Catalyst Separation Process

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

Reaction products with catalyst

The catalyst separation from the reaction products

Biodiesel Purification Process



Results

Catalyst Characterization

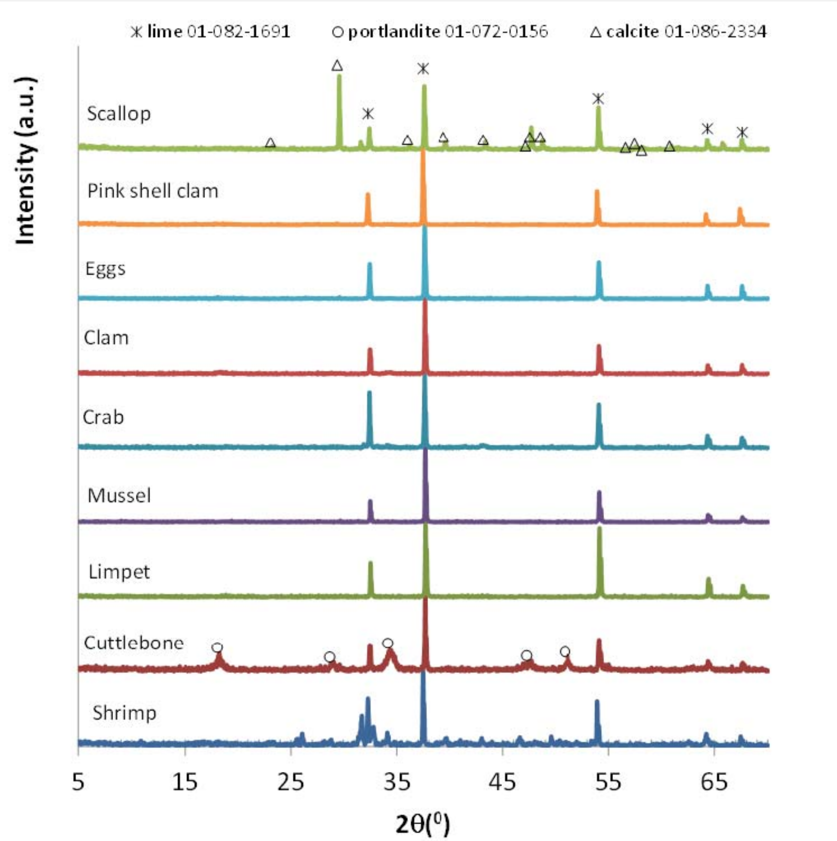


Figure 1 - XRD patterns of fresh catalysts prepared by calcination at 800ºC.
Lime: CaO; Portlandite: $Ca(OH)_2$; Calcite: $CaCO_3$.

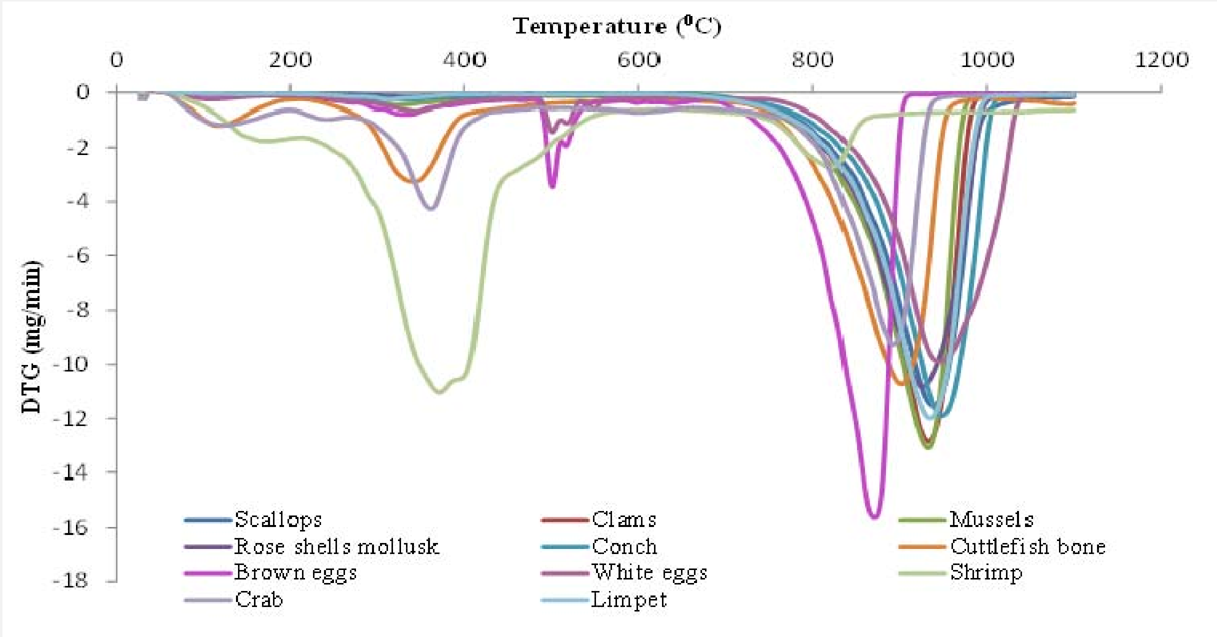


Figure 2 - Shows the DTA profiles of 9 raw Ca wastes as fresh catalysts.

Biodiesel Characterization

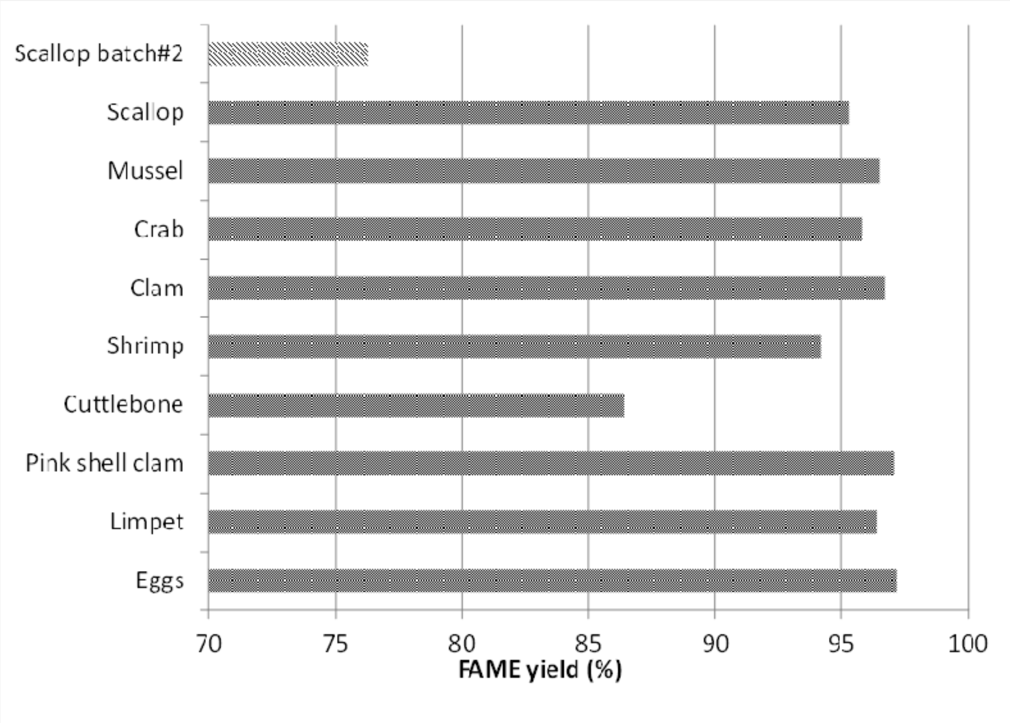


Figure 3 – FAME yield, assessed by thermogravimetry, obtained for soybean oil using the lime catalysts from Ca rich alimentary wastes (5 % w_{cat}/w_{oil}; molar racio methanol/oil=12; 2.5 h).

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

Catalyst	Raw-material	FAME yield (%)
Scallop	50%WFO_50%Soy	90.9
Shellmix		82.6
Shellmix	75%WFO_25%Soy	82.0
Shellmix batch#1	WFO	62.5
Shellmix batch#2		88.4

Conclusions

- ✓ In standard conditions high FAME yields were obtained for all the tested catalyst whith 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

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Thank You For Your Attention