NEW BIOFUELS BASED ON GLYCEROL KETAL ESTERS

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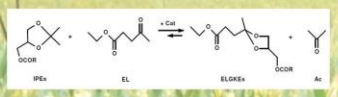
Biomass is an attractive renewable resource seen as a sustainable alternative for the production of liquid transportation fuels, thus diminishing fossil fuels need. The production of ecological fuel components derived from renewable sources increased significantly in recent years due to the harsh environmental policy promoted in many developed countries. As a result of this biodiesel and oleochemicals production booming, more than two million tonnes of glycerol consistently reach the market every year, even though the total glycerol supply is expected to slightly decrease in the near future. Ethyl levulinate is an important renewable building block, due to its rich chemistry and potential availability, from polysaccharides such as fructose, glucose, sucrose, and cellulose from biomass.

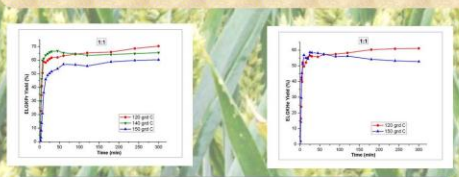
Glycerol based acetals and ketals have been identified to have particular qualities as fuel additives (improve the octane number and cold flow properties, reduce particulate emission and gum formation). In most of the studies related to glycerol processing, it is still difficult to obtain good selectivity in the desired products at high glycerol conversion, due to the wide hydroxylic functionalization of the triol glycerol molecule of similar reactivity, the unknown reaction conditions or the lack of optimum catalysts.

The purpose of this work is to report a versatile method for obtaining new glycerol acetal/ketal esters, difficult to synthesize using classical techniques, based on reactive distillation, in order to be used as diesel fuel additives.

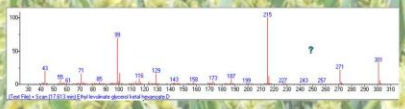
Syntheses of ethyl levulinate glycerol ketal esters (ELGKEs) were performed by reacting 1,2-O-isopropylidene-glycerol esters (IPEs) and ethyl levulinate (EL), in presence of an heterogeneous acid catalyst. Tungstophosphoric acid catalyst supported on γ-alumina extrudates was prepared and characterized by means of FT-IR, TG-DTA, XRD, EDX-TEM, and BET. Experiments were conducted in Asia 330, an integrated flow chemistry system.



Solutions consisting of IPEs and EL (IPEs and Fu are miscible) were introduced in the reactor, then heated in the range of 120-150ºC, and of influence of reaction time was studied, using the stoichiometric feed ratio. To achieve high conversions, the reaction equilibrium was displaced by continuous removal of acetone, by reactive distillation. The catalytic conversions and ELGKEs yields were determined periodically by gas chromatography (GC) of sampling small aliquots from the reactor, withdrawn at specific intervals of the total reaction time of 300 minutes.



The effect of reaction temperature on yields of ELGKPr and ELGKHe



Mass spectrum of ethyl levulinate glycerol ketal hexanoate (ELGKHe)

Confirmation of structures of the new compounds synthesized was performed by gas chromatography coupled with mass spectrometry (GC/MS), using a GC-MS/MS TRIPLE QUAD (Agilent 7890 A), and by NMR spectra recorded on a Bruker Avance DRX 400 instrument operating at 400.1 and 100.6 MHz for ^{1}H and ^{13}C.

CONCLUSIONS

A new method for obtaining glycerol acetal/ketal esters has been developed, and its viability has been proven by synthesizing new compounds having structures of ELGKEs. Due to versatility of method, it is possible to replace Ac from structures of IPGEs with both aldehydes or ketones. Recycling the heterogeneous catalyst and Ac, and avoiding the use of solvents as reaction medium should increase the eco-friendliness of this method.

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