Upgradation of fast pyrolysis oil derived from wood through Esterification

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Outlines

- Motivation
- Introduction
- Charaterisation of Bio-oil and Catalyst
- Bio-oil upgrading by catalytic Esterification
- Results and Discussion
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Motivation

- Expected fossil fuel depletion and environmental concerns leads to substantial research on renewable resource.
- Biomass derived fuels could be the prospective fuels of tomorrow.
- Biomass can be produced within short time and helps in CO_2 reduction from environment.

Introduction

- Biomass can convert into fuels using different techniques.
- Recent research on biomass conversion to fuels focuses on fast pyrolysis.
- Process that produces fuel in three different phase (Solid + liquid + gas)
- Fast pyrolysis of biomass can produce liquid fuels (pyrolysis oil or bio-oil) that can be easily stored and transported.
- Different applications of bio-oil include boiler systems, stationary diesel engines, gas turbines and sterling engines.

Charaterisation of bio-oil

Physical Properties	value	Measured using
Moisture content (wt %)	26.36	Karl Fischer titrator
pH	2.78	pH meter
Density (kg m^{-3})	1.08	Pycnometer
Elemental composition (wt %)		
Carbon	50.92	
Hydrogen	8.27	
Oxygen(by difference)	38.57	
Nitrogen	2.23	
Ash (wt %)	0.0	Thermo-gravimetric analysis
HHV (MJ kg^{-1})	22.20	
Viscosity (cP) at T=40^{o}C	73.62	Cannon-Fenske Viscometer

Challenges in using of bio-oil

- Oxygen in bio-oil: 38.57% by weight
- Causes most of the negative properties
  - Variable viscosity
  - High Moisture content
  - High acidity
  - Pungent odor
  - Low energy value

Areas Currently Being Researched

- Storage and longevity
- Low pH/ high acidity
- Immiscibility with non-aqueous liquids
- Combustion/Co-Firing
- Market Feasibility

Upgradation of bio-oil

Physical upgrading of bio-oil

Filtration → microfiltration, carried out at elevated temperatures using commercially available ceramic membranes, to removes essentially all of the char content

Solvent addition → Addition of Alcohol stabilize the Bio-oil
Ethanol, butanol decreases viscosity more rapidly

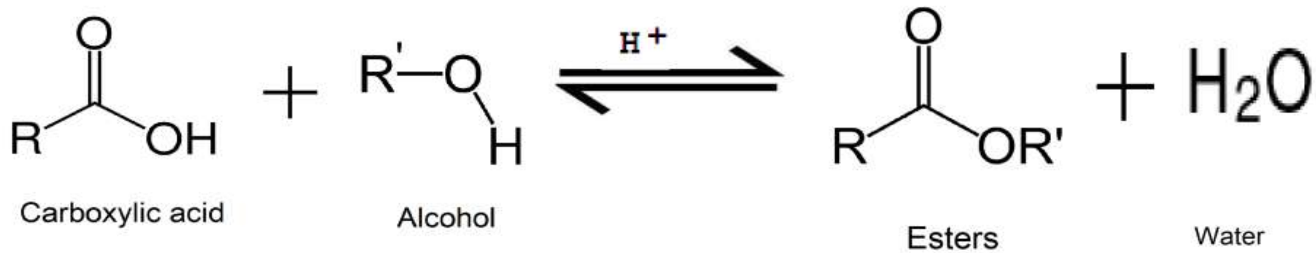
Emulsions → bio-oil is emulsified in No. 2 diesel fuel stability of emulsion depends on three factors, surfactant concentration bio-oil concentration and power input

Catalytic upgrading of bio-oil

- Hydrotreating
- Catalytic vapor cracking
- Esterification process

Upgrading of Bio-oil by Esterification

- Esterification : Conversion of an acid into an ester by combination with an alcohol and removal of a molecule of water.



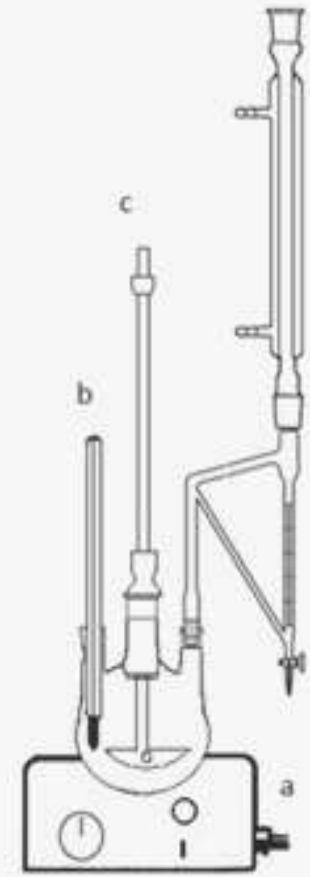
- n-butanol is selected as alcohol in our process.
- Removal of water is essential to drive the equilibria to the right side.
- Esterification reactions are acid-catalyzed.

✓ Homogeneous catalyst H_2SO_4, Heterogeneous catalyst Nafion NR-50, Amberlyst-15.

Setup and Procedure

- Equal amounts of Bio-oil and n-butanol charged into the reactor vessel
- Boil-up temperature (95-105^{o}C)
- Subsequently (10wt% of feed), Amberlyst-15 was added to reaction mixture
- The starting of the reaction was set at the time for formation of the first drop of distillate in the condenser.
- Reaction time was 150 min
- Distillate collected consists of two phases, one is organic and the other is aqueous phase.

Experimental set-up

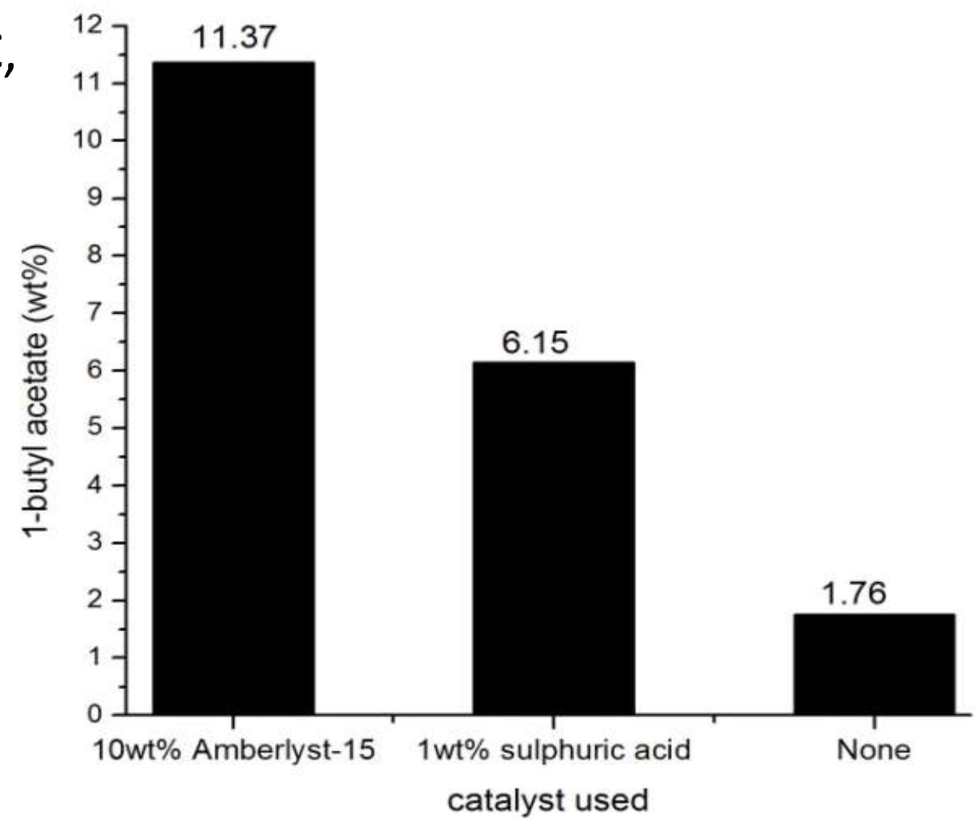


a = Heating mantle, b = Thermometer, c = Stirrer, d = Dean-stark apparatus, e = Reflux condensor

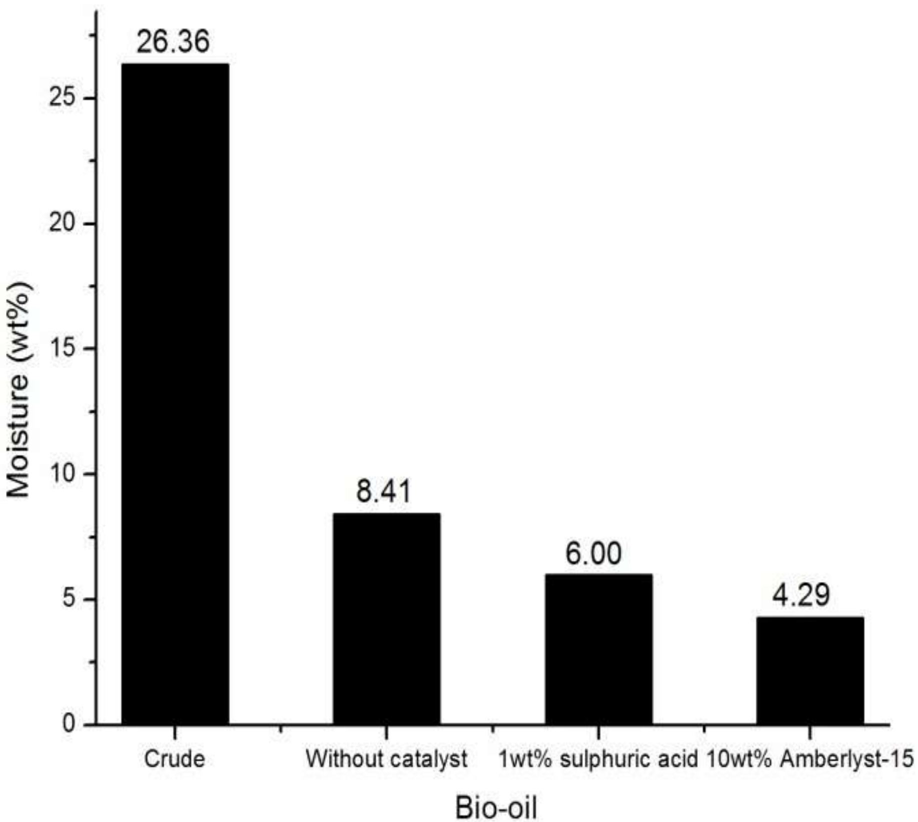
Results and Discussion

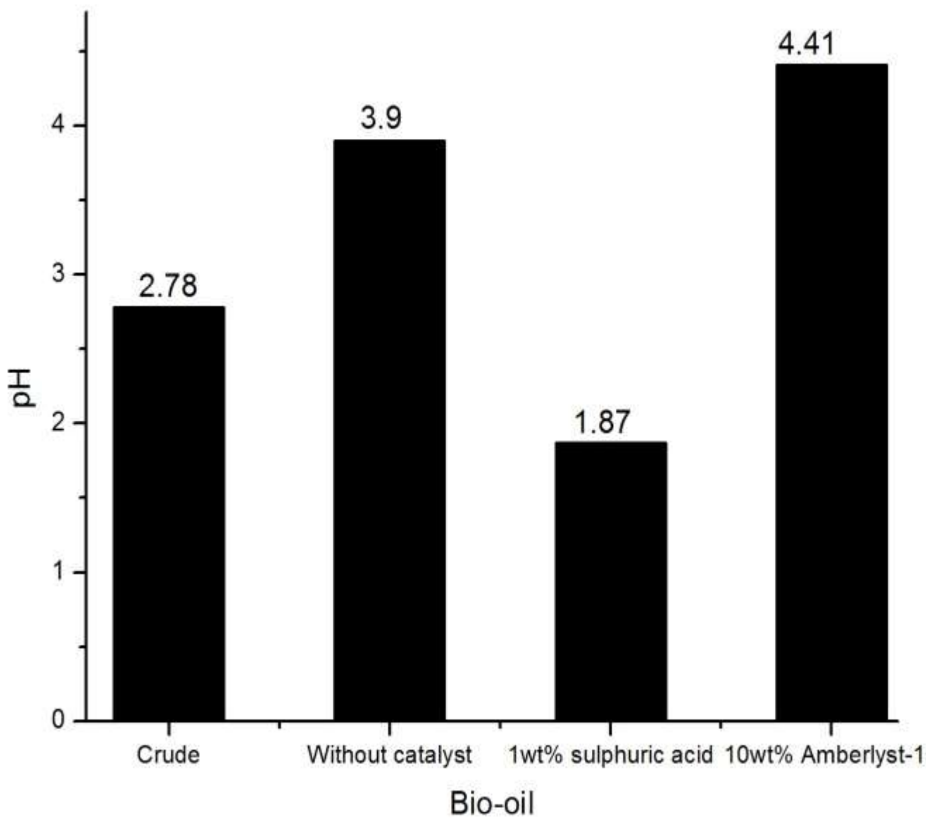
Esterification using different catalysts

- ✓Temperature range: 95-105°C,
- ✓reaction time: 150 min,
- ✓Stirrer speed: 600 RPM

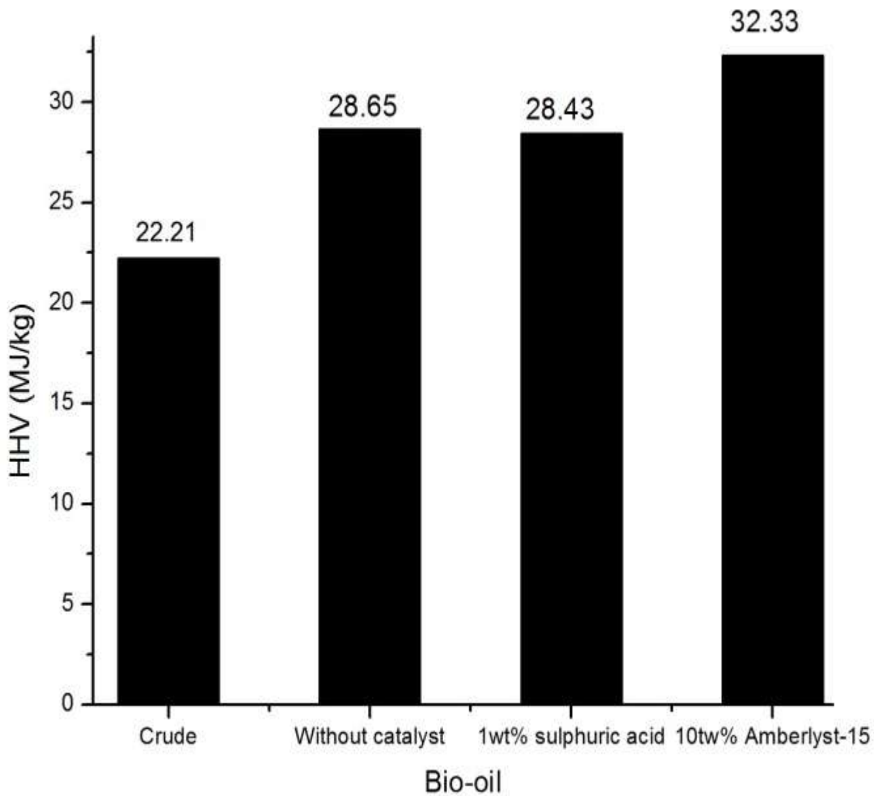


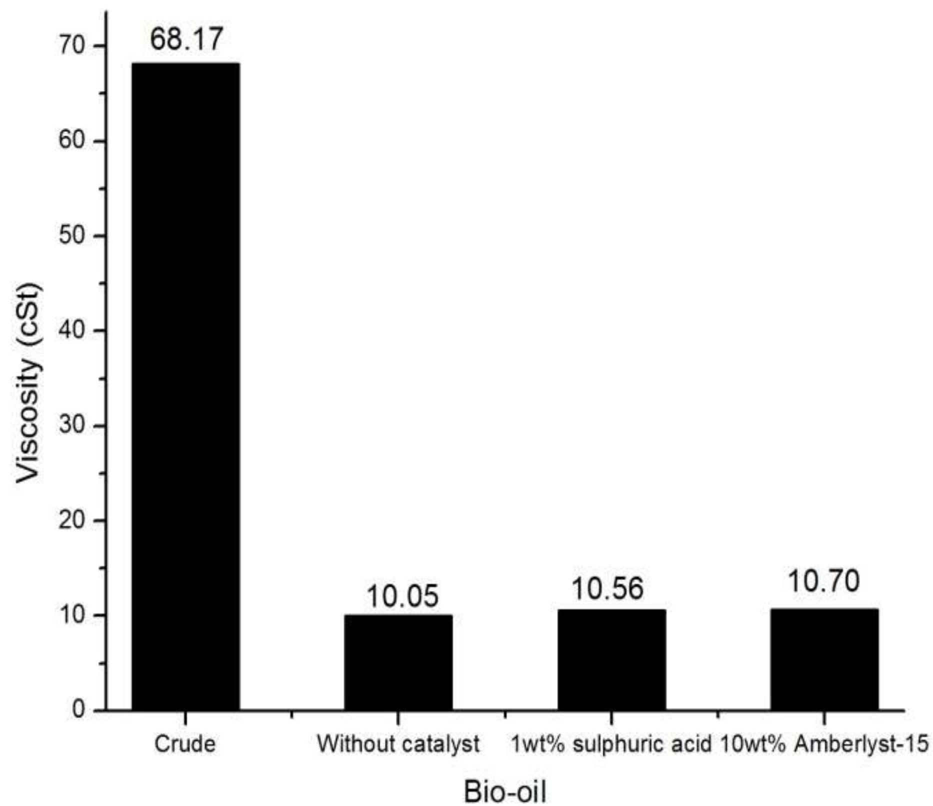
Characteristic properties of bio-oil upgraded using heterogonous and homogeneous catalysts



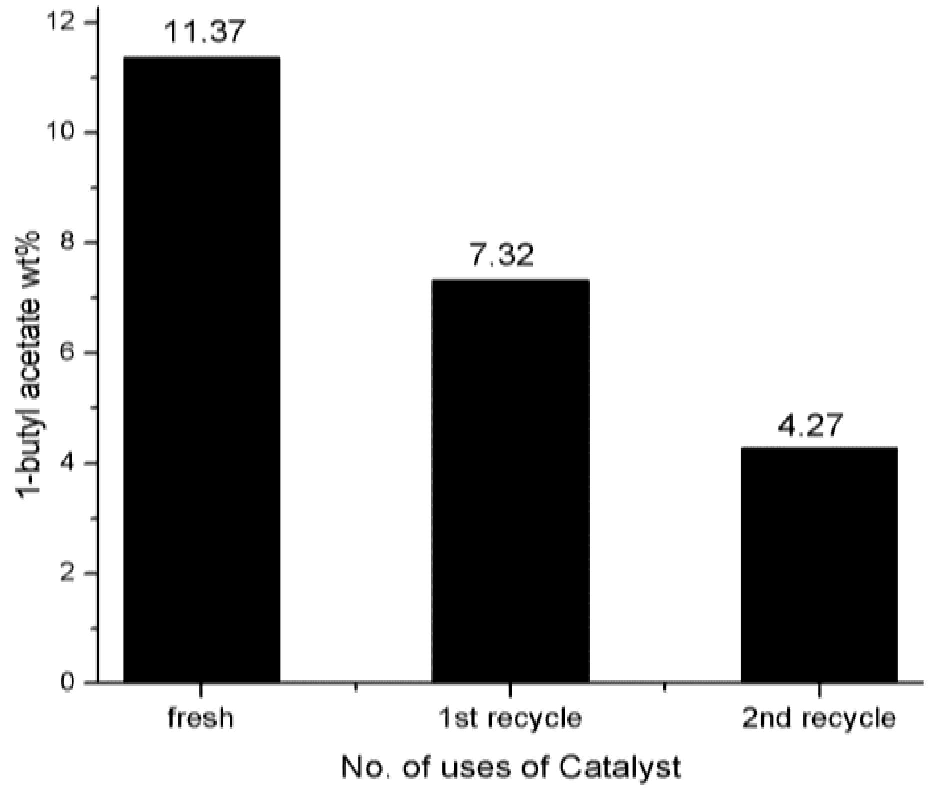


Heating value and Viscosity



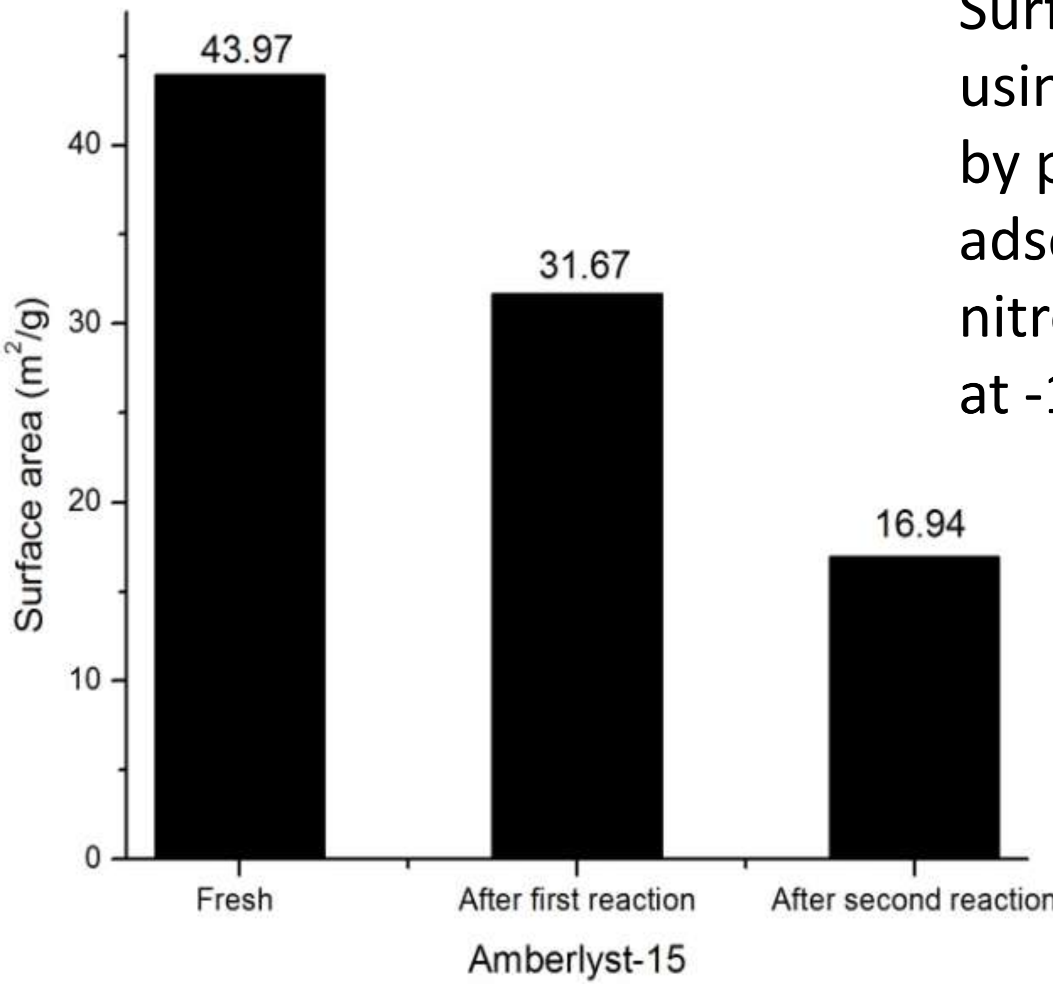


Performance of Amberlyst-15 in esterification of crude bio-oil after repeated use.



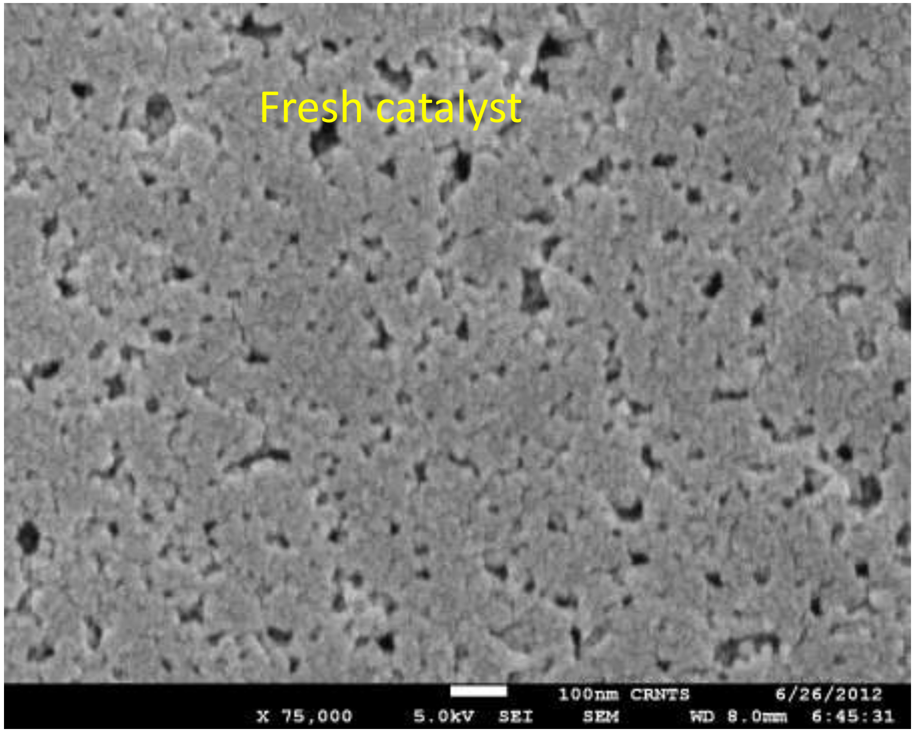
✓ To identify problems associated with catalyst deactivation, Amberlyst-15 was characterized using different analytical techniques, including FEG-SEM, BET surface area analysis and Thermogravimetric analysis

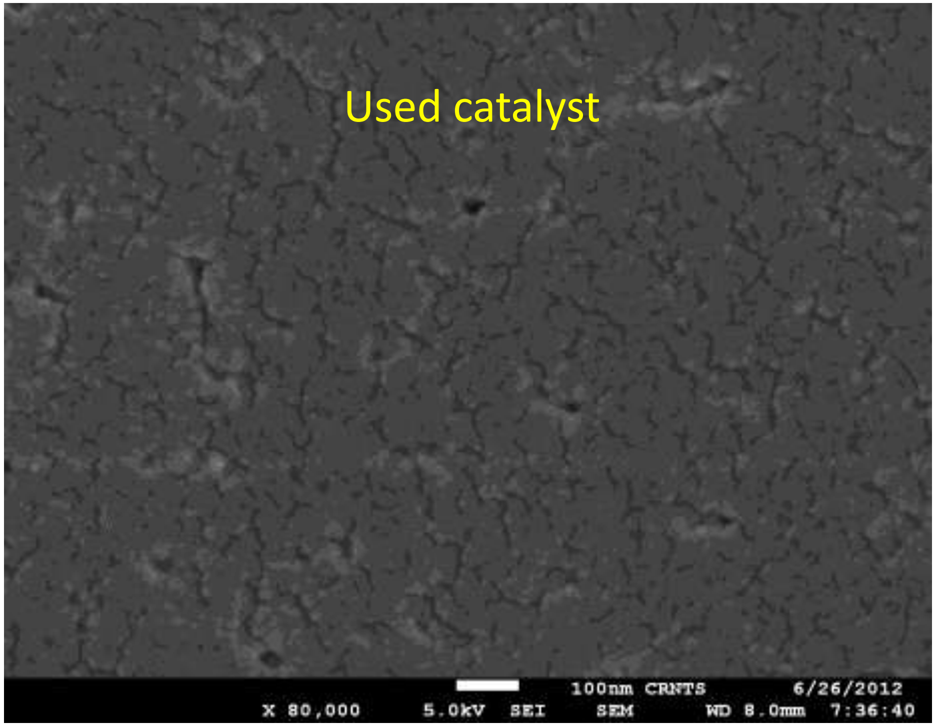
Charaterisation of catalyst



Surface area catalsyt is done using BET surface analyser by physical adsorption/desorption of nitrogen on a solid surface at -195°C

Surface morphology of catalyst

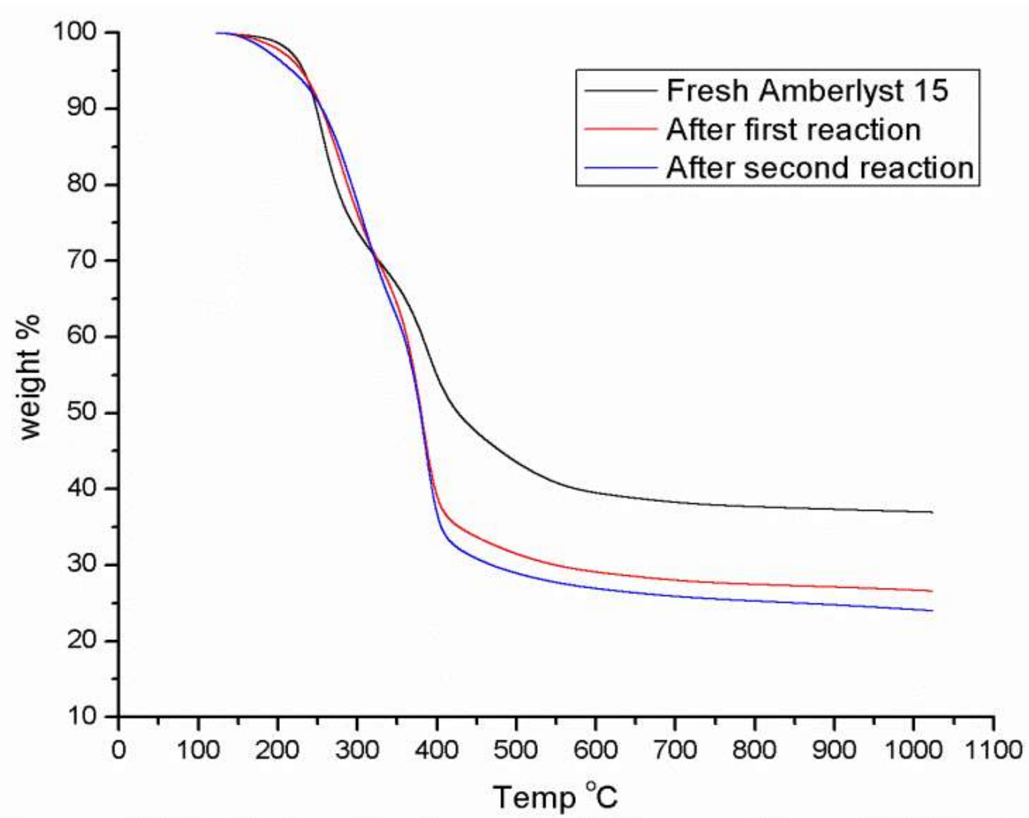




✓Surface morphology was determined using field-emission gun-scanning electron microscope

✓Observation: pores blocked by char present in bio-oil

TGA of catalyst



Change in weight % at higher temperature indicates that some volatiles are deposited on catalyst during bio-oil upgradation.

Thermo-gravimetric analysis of Amberlyst-15 was carried out over a temperature range of 120-1022^{o}C with a rate of 5^{o}C/min and under a flowing N_2 atmosphere (flow rate, 150 mL/min).

Conclusions

- Bio-oil was upgraded using n-butanol with Amberlyst-15 as catalyst.
- With this solid catalyst, the subsequent neutralization step after treatment can be avoided,
- Catalyst gets deactivated because of the deposition of carbonaceous material present in bio-oil.
- Identifying conditions under which deactivation is insignificant and possible ways to regenerate catalyst are future directions for research in this area.

Thank you