Acid catalysts used to ecological additives synthesis for fuels

PhD Coordinator — Prof. dr. ing. Dragoş Ciuparu

PhD Candidate — Ing. Viorel Voicu

The subject of this PhD thesis focuses on the glycerol etherification with isobutene over synthesed or provided acid catalysts to obtain a mixture of tert-butyl glycerol ethers derivates. The obtained ethers are used as additives for hydrotreated gasoil to establish their performance on the internal burning engine.

This PhD thesis is structured on three main important aspects concerning the synthesis of the ecological additves, distributed and developped in different chapters. First concern, the synthesis of some acid catalysts which present an optimized dimension and structure that allow a total conversion of the reagents (glycerol and isobutene). Second concern, the performances of the synthesized catalysts on glycerol etherification reaction with isobutene were determined to obtain a mixture of tert-butyl glycerol ethers derivates, then, used as ecological additives for gasoil. At the same time, the glycerol etherification reaction with isobutene was studied over different types of catalyst (solid heteropolyacid $H_4SiW_{12}O_{40}.30H_2O$ and ion exchange resins CT 175 Purolite achieved and untested catalysts on etherification process until this present study) without and in presence of emulsifiers [cationic N-tallow propylene diamine (Dinoram S), non-ionic ethoxylated alcohol C_{12}-C_{14} and amphoteric ammonium quaternary salt ($C_{19}H_{42}NBr$ şi $C_{27}H_{42}NO_2Cl$) untested until this present study] under some reaction conditions. Third concern focuses on how these additives improve the engine behaviour, also the combustion process, when using these additives-diesel blends.

Sulfonic acid supported on ordered mesoporous materials catalysts were synthesized by the pore volume impregnation method using aqueous solutions of acids. The nitrogen adsorption/desorption isotherms confirmed the type IV characteristic for the well-ordered hexagonal structure silicas and allowed determining of the pore size distribution before and after impregnation. XRD assessments proved that the amorphous hexagonal structure of the silica supports MCM-41 and SBA-15, also for the synthesized catalysts. The FT-IR spectra

gave evidence of the presence of sulfonic acid groups in the structure of the catalysts. The synthesized 8.36 wt % TFESA/MCM-41 and 8.83 wt % TFESA/SBA-15 catalysts were tested in glycerol etherification with isobutene and proved good activity leading to high conversions for both reagents (95.0 % for glycerol and 100.0 % for isobutene).

The biggest conversions for both reagents and the biggest yields in desired products over heteropolyacid $H_4SiW_{12}O_{40}.30H_2O$ catalyst were obtained in presence of the amphoteric ammonium quaternary salt C_{19} ($C_{19}H_{42}NBr$) emulsifier. The amphoteric ammonium quaternary salt C_{27} ($C_{27}H_{42}NO_2Cl$) emulsifier is the most efficient emulsifier on the glycerol etherification with isobutene in presence of ion exchange resin CT 175 Purolite catalyst, since there were obtained the biggest conversions and yields in desired products. The catalyst particles are available for promoting the glycerol etherification reaction, because the isobutene molecules surrounding the catalyst, since decreasing of viscosity of the glycerol phase by emulsification process.

After the engine tests on the Diesel engine, the study guided to the conclusion that the using of additivated diesel fuel is more advantageous; since to the diminishing of the fuel viscosity, of the flue emissions, of the CO and NO_x pollutant emissions from exhaust gas, and also by a lower variation of exhaust gas temperature.

The author gratefully acknowledges the financial support of this work from the European Social Fund through Sectorial Operational Programme of Human Resources Development (Project number POSDRU/6/1.5/S/18).