

SAŽETAK

Utjecaj vrste reaktanata i reakcijskih parametara na proces sinteze biodizelskih goriva iz viših alkohola

Istraživanje i razvoj naprednih biogoriva motiviran je smanjenjem negativnog utjecaja na okoliš uzrokovanog višestoljetnom primjenom fosilnih goriva, a potaknut i od strane zakonskih regulativa Europske Unije koje potiču energetske diverzifikaciju, dekarbonizaciju prometnog sektora te načela kružnog gospodarstva. Jedno od takvih biogoriva je i biodizel, koji se proizvodi transesterifikacijom triglicerida alkoholom, u prisutnosti katalizatora. Nakon pročišćavanja, moguće ga je namiješati s fosilnim gorivom te, ukoliko zadovolji norme za dizelsko (HRN EN 590) i biodizelsko (HRN EN 14214) gorivo, koristiti kao obnovljivi izvor energije u dizel motorima. U Republici Hrvatskoj dopušteno je namiješavanje biodizelskog s dizelskim gorivom do volumnog udjela od 7 % da bi se njihova mješavina i dalje deklarirala dizelskim gorivom. Biodizel je moguće s dizelskim gorivom namiješati i u višim volumnih udjelima, no u tom se slučaju radi o mješavinama dizelskog i biodizelskog goriva. S obzirom da se komercijalni biodizel u Europi najčešće proizvodi iz djelomično obnovljivog metanola, cilj ovog doktorskog rada bio je ispitati utjecaj vrste reaktanata i reakcijskih uvjeta na proces sinteze biodizela iz izomera različitih viših alkohola (od propanola do oktanola), koje je moguće kao bioalkohole fermentacijom u potpunosti proizvesti iz biomase. U prvom dijelu ovog doktorskog rada praćen je utjecaj reakcijskih uvjeta (temperature, vremena reakcije, molarnog omjera reaktanata te masenog udjela katalizatora) na iskorištenje reakcije transesterifikacije. Primjenom Box-Behnkenovog dizajna eksperimenta i metodologije odzivnih površina, analizirani su i optimirani sustavi u kojima je biodizel sintetiziran iz suncokretovog ulja i alkohola 1-propanola ili 1-oktanola, odnosno otpadnog ulja i sekundarnog alkohola 2-propanola, 2-butanola, 2-pentanola ili 2-oktanola, u prisutnosti kalijeve hidroksida (KOH), kao katalizatora. Dodatno, praćena je i ovisnost iskorištenja sinteze biodizela o spomenutim reakcijskim uvjetima, kemijskoj strukturi te molekularnoj masi reaktanata, u prisutnosti KOH, pri čemu su različite biosirovine bile suncokretovo, repičino, kokosovo, otpadno ulje te životinjska (svinjska) mast, koje su reagirane s 1-propanolom, 1-butanolom, izobutanolom, 1-pentanolom, izopentanolom, 1-heksanolom ili 2-heksanolom. U drugom dijelu rada, veće šarže biodizela (metilnih, propilnih, butilnih, izobutilnih, pentilnih, heksilnih i oktilnih

estera masnih kiselina) sintetizirane su iz otpadnog ulja u prisutnosti KOH, pri uvjetima najviših eksperimentalnih iskorištenja; pročišćene te namiješane u dvokomponentne i trokomponentne mješavine s neaditiviranim mineralnim dizelom i/ili odgovarajućim alkoholom. Provedena je analiza primjenskih svojstava priređenih uzoraka prema odgovarajućim normiranim metodama (gustoće, kinematičke viskoznosti, maglišta, točke filtrabilnosti, tecišta, mazivosti, simulirane destilacije), čije su vrijednosti uspoređene s onima propisanim normom za dizelsko gorivo HRN EN 590. Dodatno su uzorci analizirani metodama: diferencijalna pretražna kalorimetrija, mjerenje napetosti površine goniometrom i mjerenje koeficijenta trenja. Glavni rezultati su pokazali da su za iskorištenje ovih reakcijskih sustava značajni reakcijski uvjeti molarni omjer reaktanata i maseni udio katalizatora KOH, odnosno da se u promatranim sustavima, generalno najviša iskorištenja dobivaju korištenjem kokosovog ulja, a najniža korištenjem životinjske masti, kao biosirovine. Iskorištenja biodizela sintetiziranih iz ravnolančanih alkohola generalno su bila viša od onih sintetiziranih iz granatih, a porast molekulske mase granatih alkohola dovodi do daljnjeg sniženja iskorištenja. Karakterizacijom uzoraka utvrđeno je da dodatak biodizelskih goriva do 20 vol.% u mješavine s dizelom i/ili pripadajućim alkoholom rezultira porastom njihove gustoće, kinematičke viskoznosti i površinske napetosti, dok dodatak viših alkohola do 15 vol.% u odgovarajuće mješavine s dizelom i biodizelom rezultira smanjenjem njihove gustoće, kinematičke viskoznosti i površinske napetosti. Vrijednosti gustoća i kinematičkih viskoznosti za sve dvokomponentne mješavine dizel-biodizel (s do 20 vol.% biodizela) te trokomponentne mješavine dizel-biodizel-pripadajući alkohol (s do 15 vol.% biodizela) nalaze se unutar granica propisanih normom za dizelsko gorivo HRN EN 590. Nadalje, namiješavanjem biodizelskih goriva i/ili odgovarajućih alkohola s mineralnim dizelom nije došlo do narušavanja njegovih nisko-temperaturnih svojstava (maglišta, točke filtrabilnosti, tecišta). Reološkim mjerenjima utvrđeno je da dodatak heksilnih estera masnih kiselina neaditiviranom mineralnog dizelu u količini od 2,5 vol.% značajno poboljšava njegovu mazivost, dok promjena udjela ili vrste biodizela namiješanog s mineralnim dizelom nema značajnog utjecaja na svojstva podmazivanja dizelskog goriva. Napoljetku, uočeno je da su za destilaciju istog postotka predestiliranog, dodatkom pentilnih estera masnih kiselina od 20 vol.% mineralnom dizelu, potrebne više temperature nego u slučaju dodatka istog biodizela u udjelu od 10 vol.%. Diferencijalna pretražna kalorimetrija pokazala je da dvokomponentne i trokomponentne mješavine svih biodizela s mineralnim dizelom i/ili pripadajućim alkoholom imaju temperature početke i kraja kristalizacije slične vrijednostima onih

neaditiviranog mineralnog dizela. Navedeno može poslužiti kako dodatni pokazatelj izostanka njihova negativnog djelovanja na niskotemperaturna svojstva dizelskog goriva.

Ključne riječi: biodizel, transesterifikacija, nuklearna magnetska rezonancija, dizajn eksperimenta prema Box-Behnken, metodologija odzivnih površina, optimizacija, primjenska svojstva, normirane metode

ABSTRACT

Influence of the type of the reactants and reaction parameters on the synthesis of biodiesel fuels from higher alcohols

The research and development of advanced biofuels is motivated by the reduction of negative environmental impact caused with the use of fossil fuels throughout the centuries, and encouraged with the legal regulations of European Union, that promote energy diversification, decarbonization of the traffic sector, as well as the principles of circular economy. One of such biofuels is biodiesel, that is produced via alcohol transesterification of a certain feedstock, in the presence of a catalyst. Post purification, it is possible to blend it with fossil fuel, if it fulfills the requirements set by the diesel (HRN EN 590) and biodiesel (HRN EN 14214) standard, and use as a renewable source of energy in diesel engines. In the Republic of Croatia it is allowed to blend up to 7 vol% of biodiesel with diesel fuel for their blend to still be declared as diesel fuel. It is possible to blend higher volume fractions of biodiesel fuel with diesel fuel, as well, however these are referred to as the diesel-biodiesel blends. Since the commercial European biodiesel is most commonly produced from partly renewable methanol, the goal of this doctoral thesis was to investigate the influence of the reactant type and the reaction conditions on the biodiesel synthesis from isomers of selected higher alcohols (from propanol to octanol), which can, as bioalcohols, be completely produced via fermentation from biomass. In the first part of this doctoral thesis, the influence of reaction conditions (temperature, reaction time, molar ratio of the reactants, and mass fraction of the catalyst) on the reaction conversion of the biodiesel systems, was studied. With the use of Design of Experiments by Box-Behnken and Response Surface Methodology, the biodiesel synthesis from either sunflower oil and alcohols 1-propanol or 1-octanol, or waste cooking oil and 2-propanol, 2-butanol, 2-pentanol, or 2-octanol, was analyzed and optimized, in the presence of a catalyst potassium hydroxide. Additionally, the dependence of the reaction conversion on the mentioned reaction conditions, the chemical structure, and the molar mass of the reactants, in the presence of potassium hydroxide, was studied, with the selected feedstock being sunflower oil, rapeseed oil, coconut oil, waste cooking oil, or animal fat, that reacted with 1-propanol, 1-butanol, isobutanol, 1-pentanol, isopentanol, 1-hexanol, or 2-hexanol. In the second part of the thesis, larger amounts of biodiesels (fatty acid methyl, propyl, butyl, isobutyl, pentyl, hexyl, and octyl esters) were

synthesized from waste cooking oil, in the presence of KOH, at the conditions of the highest experimental conversions; purified, and blended into the binary and trinary blends with non-additivated mineral diesel and/or corresponding alcohol. The prepared samples underwent the application property analysis via corresponding standardized methods (density, kinematic viscosity, cloud point, cold filter plugging point, pour point, lubricity, simulated distillation), the results of which were compared with the ones prescribed by the standard for diesel fuel HRN EN 590. Additionally, samples were analyzed via instrumental analytical methods: differential scanning calorimetry, surface tension measurements via goniometer, and friction coefficient measurements. The main results showed that the most significant reaction conditions in the given systems were the molar ratio of the reactants, and the mass fraction of the catalyst KOH, and that in the selected systems experimentally the highest conversions were obtained using coconut oil, while the lowest using animal fat, as a feedstock. The reaction conversions in the synthesis using straight-chain alcohols were generally higher than those with branched alcohols, and the increase in the molecular weight of branched alcohols further led to a decrease in the conversion. Sample characterization determined the addition of selected biodiesel fuels up to 20 vol% into the blends with mineral diesel and/or corresponding alcohol led to the increase in their density, kinematic viscosity, and surface tension, while the addition of the selected higher alcohol up to 15 vol% in the blends with diesel and biodiesel resulted in the reduction of their density, kinematic viscosity, and surface tension. Density and kinematic viscosity values of all the binary diesel-biodiesel (with up to 20 vol% of biodiesel), and trinary diesel-biodiesel-corresponding alcohol blends (with up to 15 vol% of biodiesel) were within the limits required by the standard for diesel fuel HRN EN 590. Furthermore, blending of selected biodiesels and/or corresponding alcohols with mineral diesel did not aggravate its analyzed low-temperature properties (cloud point, cold filter plugging point, pour point). Rheological measurements determined that the addition of fatty acid hexyl esters to non-additivated mineral diesel of just 2.5 vol% significantly improved its lubricity, whereas the change in the volume fraction or the type of biodiesel blended with mineral diesel did not have a significant influence on the diesel's lubricating properties. Finally, it was observed that for the distillation of the same percentage of the sample, the higher temperatures were required with the addition of fatty acid pentyl esters of 20 vol% to mineral diesel, than with the addition of the same biodiesel in the volume fraction of 10 vol%. On the other hand, differential scanning calorimetry showed that the binary and trinary blends of all biodiesels with mineral diesel and/or corresponding

alcohol had onset and peak crystallization temperature values close to the ones of non-additivated mineral diesel. This could serve as an additional indicator for the lack of their negative impact on the diesel's low-temperature properties.

Keywords: biodiesel, transesterification, nuclear magnetic resonance, Box-Behnken experimental design, response surface methodology, optimization, application properties, standardized tests