Abstract

Waste treatment and valorization is a strategy whereby a few of the sustainable development goals focused on affordable, reliable, inexhaustible, clean energy and crusade against climate change and its effects could be actualized. Utilization of coal fly ash (CFA) and waste industrial brine (WIB) to synthesize a heterogeneous solid catalyst such as hydroxy sodalite (HSOD) that could be used to convert other waste materials (animal fat oil (AFO) and waste cooking oil (WCO)) to biofuels including biodiesel (BD) is a promising approach to waste treatment and valorization. In this thesis, the use of CFA and WIB obtained from the vicinity of coal-fired power plants in South Africa in producing solid HSOD catalyst and the use of the catalyst in transesterifying AFO into BD is demonstrated via hydrothermal technique. Previous studies reveal that the activity of solid HSOD synthesized from non-waste precursors has proven good candidacy for catalytic application in biodiesel production using waste cooking oil. It was however, observed that the performance of the non-waste catalyst particles was plagued by low surface area and pore volume. Enhancement of the specific surface and the pore volume, and optimization of the synthesis protocol of the waste-derived catalyst may overcome these difficulties. In this study, synthesis, optimization and performance evaluation of waste-derived solid hydroxy sodalite catalyst prepared from waste was characterized using different characterization techniques. The prepared waste-derived catalyst was evaluated for catalytic performance tests for the transesterification of WCO and AFO to biodiesel. Effect of operating variables on biodiesel production over waste solid HSOD catalyst was carried out. Prediction of biodiesel yield using artificial neural networks (ANNs) was investigated. Also explored, was the kinetic study of the synthesized waste-derived HSOD catalyst in the conversion of AFO to biodiesel in a batch and fixed bed reactors. An economic assessment of biodiesel production with the waste-derived HSOD as a preliminary study was elucidated in a two catalyst production scenarios. Experimental results of the study reveal that South African CFA belongs to the class F and the transformation of the CFA and WIB into HSOD catalyst yielded HSOD of silicon/aluminium (Si/Al) ratio of 1.24 with a surface area of 33.05 m^2g^{-1}. This study shows that the surface area of the waste-derived catalyst is considerably enhancement when compared with the original surface area (0.16 m^2g^{-1}) of non-waste derived HSOD catalyst synthesized using pure chemicals from chemical suppliers. The experimental results that favoured the optimized synthesized waste-derived HSOD catalyst were high purity, crystallinity, Si/Al ratio of 1.26,

CFA+WIB : NaOH = 1:7, hydrothermal temperature of 140 ^{o}C, reaction time of 48 h, enhanced textural properties (specific surface area and pore volume) of 4.59 m^2g^{-1} and 0.034 cm^3g^{-1}, respectively, compared to that of the non-waste HSOD catalyst of 0.16m^2g^{-1} and 0.001cm^3g^{-1}, for specific surface area and pore volume. Also, 3.5M NaOH favoured the waste-derived HSOD production. In a catalytic performance test, the yield of biodiesel was 98 % and the conversion of animal fat oil to biodiesel was 95 % when compared to the activity of the non-waste reference catalyst which was lower. Studying the effect of operating variables including alcohol-to-AFO molar ratio, amount of catalyst, reaction time, reaction temperature, agitation speed, and catalyst particle on the reactivity of this catalyst during biodiesel production in a batch reactor established process set points for each variable. Prediction of BD yield via the application of Artificial Neural Network (ANN) modelling approach resulted in biodiesel yield of 98 %. From the ANN model result, the architecture built using the 20 number of neurons in the hidden layer gave the best result. The mean square error (MSE) obtained using input variable representative technique-visual inspection method (IVRT-VIM): ***Option 2*** consisting of RT [reaction temperature], RTm [reaction time], and AtO [alcohol-to-oil/fat] as the input variables and was improved by 99.94 % and 99.93 % when compared to that of ***option 1*** consisting of RTm, RT, AtO, AC (amount of catalyst), and Ss (spinning speed) as input variables. It was established that ***option 1*** which has a combination of input variables RTm, RT and AC has higher enhancement than ***option 2*** that has a combination of input variables RTm, RT, AtO and AC. The IVRT-VIM for ***option 1*** was found to be around 94. 81 % enhancement over ***option 2***.The predicted result agrees with the experimental data (based on the fitting data), hence; indicating that the IVRT-VIM technique is promising for ANN model improvement. Result of the kinetic study of the waste-derived HSOD catalyst during the transesterification of AFO to biodiesel which was assumed as a pseudo-first order transesterification reaction is a first-order. The activation energy and the pre-exponential factor obtained were 58554.65$Jmol^{-1}$ and 2.83 min^{-1} respectively, while the rate constants determined at temperatures of 49 ℃, 57 ℃, and 62 ℃ were found to be 7.86 x 10^{-3} min^{-1}, 12.55 x 10^{-3} min^{-1} and 18.59 x 10^{-3} min^{-1} respectively. At 62 ^{o}C and 120 minutes, the optimum produced biodiesel yield reached 90 % and 93 % triglyceride (AFO) conversion was obtained. In this case, the high conversion of AFO and yield of biodiesel are attributed to enhanced textural properties and purity of the waste-derived HSOD catalyst. The catalyst is tolerant to the exceedingly high AFO free fatty acid content (24.69 mg-KOH g^{-1}) due to absence of saponification. This, in turn favoured high catalytic activity and high biodiesel yield. A kinetic reaction model was developed for describing the overall process. An Eley-Rideal model reaction mechanism was able to describe the kinetic performance of transesterification catalyzed by waste-derived HSOD catalyst from AFO to animal fat oil fatty acid methyl ester (AFOFAME) in a fixed bed reactor (FBR), and the kinetic parameters were compared with that of the batch which indicate that the waste-derived HSOD catalyst displayed higher catalytic activity (higher conversion) in the transesterification of AFO to AFOFAME in the FBR than in the batch reactor. This resulted in lower activation energy of 30903.30 $Jmol^{-1}$ and higher reaction rate constant of 0.0194 min^{-1} for the FBR. An economic assessment of biodiesel production using the waste-derived HSOD and a sulphuric acid homogeneous catalyst indicated a higher and positive return on investment using the waste-derived HSOD over the homogeneous catalyst. About 98 % biodiesel yield was obtained. This agrees with the ANN model result. In conclusion, this research focused on Synthesis, optimization and performance evaluation of waste-derived solid sodalite catalyst for the transesterification of animal fat oil to biodiesel. The aim of the research was to derive value-added products (catalysts and biodiesel) from four major wastes (coal fly ash, waste industrial brine, waste cooking oil and animal fat) which have potential to cause immense environmental pollution. An integrated approach to the management of these wastes, which focuses on energy recovery have potential significant economic and environmental impact. The investigation conducted is typical, addressing the issue of energy security. It further, tackles catalysis and the food versus fuel debate that have been major bottlenecks to the production of biodiesel. This investigation provides an in-depth knowledge and novelty necessary for the development of sustainable process which will enhance throughputs in the bioenergy research and industry.