



Research article

The potential of K_3PO_4 , K_2CO_3 , Na_3PO_4 and Na_2CO_3 as reusable alkaline catalysts for practical application in biodiesel production

Kristaps Malins

Riga Technical University, Institute of Applied Chemistry, Paula Valdena Str. 3, Riga LV-1048, Latvia



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ABSTRACT

K_3PO_4 , K_2CO_3 , Na_3PO_4 and Na_2CO_3 performance in biodiesel production by transesterification reaction of rapeseed oil (RO), recovery, behavior in polar alcohols (methanol, glycerol) and air during storage were studied. The catalysts were characterized by N_2 sorption analysis, XRF and FE-SEM. Potassium salts and NaOH used as reference have higher solubility in reaction mixture and activity on biodiesel production process, but significantly lower catalyst recovery and stability in air during storage than sodium salts. 88.2% of Na_3PO_4 and 87.3% of Na_2CO_3 initial amounts were recovered after transesterification process by developed method. Rest of Na_2CO_3 (11.8%) dissolved in crude glycerol can be extracted from its ashes. The effects of molar ratio of RO to methanol (1/5–1/14), reaction temperature (40–65 °C) and catalyst amount (1–7%) on Na_3PO_4 and Na_2CO_3 catalyzed transesterification were investigated. These salts can be reused up to second and fifth run without regeneration to reach > 96% of rapeseed methyl ester (RME) content in biodiesel sample under recommended conditions.

1. Introduction

The biodiesel has become one of the most promising renewable and biodegradable large scale biofuel manufactured in many countries using widely available feedstock and relatively simple production technologies. The major fuel properties of biodiesel are close to conventional diesel fuel [1]; therefore, it has been successfully used for most ordinary diesel engine exploitation. Biodiesel production capacity and consumption for transport considerably increased worldwide since its commercialization. It can be manufactured from various animal and vegetable oil fatty acids and their glycerides containing raw materials in catalytic esterification or transesterification reaction with alcohols [2]. Generally feedstocks, catalysts and technologies utilized for biodiesel production determine sustainability and profitability of the overall process [3]. Commonly the biodiesel has been produced from food grade vegetable oils such as soybean (USA), rapeseed (EU) and palm oil (tropical countries) in transesterification reaction with methanol or ethanol in presence of homogeneous alkali catalysts. Hydroxides NaOH, KOH and methoxides $NaOCH_3$, $KOCH_3$ are the most active homogeneous catalysts for biodiesel production [4, 5]. The market prices of commercial methoxide solutions in methanol are significantly higher than hydroxides, but they are more superior catalysts for biodiesel production, because they contain methoxide ions (CH_3O^-) in high concentration without presence of water. Alkali metal hydroxide

reaction with methanol is linked with formation of CH_3O^- and particular amount of water [6, 7]. Even low amount of water in reaction mixture has negative impact on alkali-catalyzed transesterification process, thus decrease overall yield of biodiesel by saponification reactions of fatty acid esters in feedstock (animal or vegetable oil) and product (biodiesel).

The homogeneous alkali catalysts have high activity on transesterification reactions, but their recovery and reusability after transesterification process is complicated, due to absolute dissolution in reaction mixture [8]. This is the main disadvantage of homogeneous catalysts. Therefore, there are various alkaline inorganic salts, which have been considered as heterogeneous catalysts for biodiesel production. CaO is the inexpensive large scale industrial product with wide application and one of the most studied heterogeneous alkaline catalysts in first and second generation biofuel synthesis field. Limestone is the general feedstock for CaO industrial production, but it also can be obtained from different biomass wastes [3, 9]. Calcination of limestone or biomass wastes with high fraction of $CaCO_3$ is common method for CaO catalyst preparation. Both types of CaO feedstocks contain particular amount of $MgCO_3$ and presence of by-product MgO after calcination process in the catalyst is inevitable. MgO has significantly lower activity on transesterification process in comparison to CaO [10]. Therefore, the modification of MgO performed by numerous researchers is important to increase its catalytic performance [11].

E-mail addresses: kristaps.malins@rtu.lv, mkrist@inbox.lv.

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Alkaline salts K_3PO_4 , Na_3PO_4 and K_2CO_3 , Na_2CO_3 similarly to CaO and MgO are inexpensive large scale industrial inorganic products widely used in various areas. These salts have sufficient basic strength to catalyze the transesterification reaction of fatty acid glycerides with alcohols. Na_3PO_4 [5] and K_3PO_4 [12, 13] possess high catalytic activity on biodiesel production process, but they deactivate after several transesterification reaction cycles. It was explained with formation of alkali metal hydrogen phosphates KH_2PO_4 , K_2HPO_4 , NaH_2PO_4 and Na_2HPO_4 from K_3PO_4 and Na_3PO_4 during transesterification process [14, 15]. The catalytic performance of alkali metal hydrogen phosphates was almost negligible in comparison to Na_3PO_4 and most active K_3PO_4 .

KOH and NaOH have been considered as promising CO_2 chemical absorbers for industrial processes, but produced carbonates K_2CO_3 and Na_2CO_3 are difficult to regenerate into initial hydroxides due to high thermal stability [16]. The impact of K_2CO_3 and Na_2CO_3 as alkaline catalysts have been widely investigated by numerous researchers on thermo-chemical conversion processes of lignocellulosic feedstocks [17, 18]. These carbonates loaded on MgO [11], Al-Ca hydrotalcite [19], cinder [20], alumina/silica [21], $\gamma-Al_2O_3$ [22] and other inorganic supports also can be used as effective solid catalysts for biodiesel production. Furthermore, K_2CO_3 and Na_2CO_3 can be easily converted into K_3PO_4 and Na_3PO_4 in reaction with H_3PO_4 . However, the comprehensive information about pure K_2CO_3 and Na_2CO_3 salt utilization as catalysts for biodiesel synthesis in research literature are not reported. Besides, K_3PO_4 , K_2CO_3 , Na_3PO_4 and Na_2CO_3 recovery data from reaction mixture after transesterification process are insufficient to evaluate their feasibility for practical application as reusable alkaline catalysts in biodiesel manufacturing. Present study is devoted to investigation of anhydrous K_3PO_4 , K_2CO_3 , Na_3PO_4 and Na_2CO_3 salt feasibility for utilization as reusable alkaline catalysts in biodiesel production process from rapeseed oil (RO) and methanol. Separation of catalyst from crude glycerol layer after transesterification reaction by dilution/washing with methanol, centrifugation and drying was used as the main method for determination of catalyst recovery. Rest of catalyst amount dissolved in crude glycerol was extracted from its ashes after burning of the sample for evaluation of overall catalyst recovery. The reusability in six transesterification reaction cycles for alkaline salts (Na_3PO_4 and Na_2CO_3) with the highest recovery and stability in air during storage were investigated. The effects of catalyst amount (1–7% of RO amount), molar ratio of RO to methanol (1/5–1/14) and reaction temperature (40–65 °C) on rapeseed oil fatty acid methyl ester (RME) production by transesterification reaction were determined. Obtained effects on transesterification reaction were compared with process performed in the presence of common homogeneous biodiesel catalyst NaOH.

2. Materials and methods

2.1. Materials

NaOH (assay 98.6 wt%), methanol (assay 99.8 wt%, water content ≤ 0.1 wt%), $Na_3PO_4 \cdot 12H_2O$, anhydrous K_2CO_3 and Na_2CO_3 (assay ≥ 98 wt%) were supplied from Lach-Ner, Chempur, Roth, Acros organics and Alfa Aesar, respectively. Concentrated HCl (35.7 wt%), anhydrous K_3PO_4 (assay ≥ 98 wt%), derivatization reagent *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA), analytical standards tricaprinn, 1,2,4-butanetriol, methyl heptadecanoate, methyl esters of stearic, palmitic, oleic, linoleic and α -linolenic acid for GC analysis were purchased from Sigma-Aldrich. The refined RO delivered from local food grade vegetable oil producer Iecavnieks & Co was used in experiments. The main characteristics of RO are given in Table 1.

2.2. Catalyst pretreatment

$Na_3PO_4 \cdot 12H_2O$ was thermally decomposed to anhydrous salt at 250 °C for 6 h. Anhydrous K_3PO_4 , K_2CO_3 , Na_3PO_4 and Na_2CO_3 were

Table 1

The main characteristics of rapeseed oil (RO).

Monoglycerides, wt%	0.3
Diglycerides, wt%	0.6
Triglycerides, wt%	98.2
Saponification value, mg KOH/g	190.7
Acid value, mg KOH/g	0.18
Water content, wt%	0.03
Fatty acid composition, wt%	
Palmitic acid (C16:0)	5.3
Stearic acid (C18:0)	1.2
Oleic acid (C18:1)	63.6
Linoleic acid (C18:2)	21.8
α -Linolenic acid (C18:3)	6.7
Other fatty acids	1.4

grinded, sieved until particle size was ≤ 0.1 mm. Directly before catalytic tests and other experiments alkaline salts were dried again at 250 °C for 2 h to completely eliminate traces of absorbed moisture and formed water of crystallization, when catalysts were grinded and sieved in air atmosphere. The main characteristics of catalysts were determined after treatment procedures.

2.3. Characterization of catalysts

The behavior of anhydrous K_3PO_4 , K_2CO_3 , Na_3PO_4 and Na_2CO_3 (0.4 g) in contact with polar solvents methanol and glycerol/methanol (weight ratio 1/3) solution was investigated for visual evaluation and prediction of catalyst solubility in alcohols and reaction mixture. 7.5 and 8.0 parts of methanol and glycerol/methanol solution to 1 part of catalyst were used in tests. The catalysts and solvents were mixed at room temperature with magnetic stirrer in screw threaded flat-bottom vials (4 ml) for 1 h. After magnet removal the mixtures were centrifuged at 3000 rpm for 10 min in the same sample vials. Then the mixtures were allowed to stay at ambient temperature for 24 h before visual evaluation of catalysts solubility in polar solvents.

Behavior tests of the anhydrous alkaline catalysts (2.0 g) in air atmosphere were performed in glass Petri dishes (40 × 12 mm) to determine their stability during storage. The catalysts were stored at ambient air humidity 28–35% and temperature 20.8–23.4 °C for 648 h. The samples were weighted after 24, 48, 120, 216, 360, 504 and 648 h by precision electronic balances (Precisa Gravimetrics) with accuracy 0.0001 g. Increase of sample weight was used as parameter for evaluation of moisture and gas absorption from air atmosphere. Identical test also were conducted with industrial biodiesel catalyst NaOH to compare the results.

The surface morphology of the anhydrous alkaline catalysts was investigated by a field emission scanning electron microscope (FE-SEM) MIRA LMU (Tescan). FE-SEM was operated at 30.0 kV of an accelerating voltage.

N_2 sorption analysis of anhydrous alkaline catalysts was performed with a Quadrasorb SI surface area and pore size analyzer at -195.85 °C (Quantachrome Instruments). The specific surface areas were determined using multipoint Brunauer–Emmett–Teller (BET) method based on the adsorption data in the relative pressure (P/P_0) range of 0.05–0.30. The total pore volumes were estimated from the amount of N_2 adsorbed at P/P_0 of 0.99.

Fresh and recovered powdery catalyst samples were analyzed by Supermini bench-top sequential wavelength dispersive X-ray fluorescence (XRF) spectrometer (Rigaku) in He atmosphere. Normalized contents of dominant elements in fresh catalyst were used as reference and compared to samples recovered after transesterification reaction. Contents were calculated from XRF intensities and analytical apparatus factory calibration data for certain element. Analysis data are relative

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