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Solid Green Biodiesel Catalysts Derived from Coal Fly Ash

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Abstract

Coal fly ash (CFA) is generated during the combustion of coal for energy production. Many studies are based on its utilization as the most abundant, cheap aluminosilicate industrial residue, which is recognized as a risk for the environment and human health. The present review is focused on CFA origin, chemical properties, and its catalytic application for biodiesel production. The aluminosilicate nature and the presence of rare earth elements make CFA suitable for different adsorption, catalytic, and extraction processes for obtaining valuable products including alternative fuels and pure elements. However, the presence of toxic elements is a potential environmental problem, which should be solved in order to avoid soil, water, and air pollution. The most used modification methods are alkali activation, hydrothermal, and thermal treatment that improve the structural, morphological, and textural properties. The active catalytic form could be obtained by impregnation or ion exchange method. It was found that such synthesized materials have significant catalytic potential in the biofuel chemistry. In the case of biodiesel production, the high values of conversion or yield can be achieved under mild low-energy reaction conditions in the presence of low-cost waste-based catalysts.

Keywords: coal fly ash, waste materials, zeolites, catalyst, transesterification, biodiesel

1. Introduction

In recent decades, we have witnessed more and more stories about energy, energy efficiency, fossil fuels reserves, and alternative energy sources. The dependence of the world on the fossil fuels is a topic of discussion by many scientists, researchers, and environmental activists worldwide. Biodiesel, as a biofuel, with numerous advantages (biodegradability, lower content of CO₂, SO₂, and hydrocarbons during combustion, high flash point, high lubricant properties, and high octane number) is a serious competitor to fossil diesel [1, 2]. Also, very important is the fact that biodiesel obtained in accordance to standard does not require modification of existing diesel engine [3]. Modern science and chemical technology know the following concepts of biodiesel production: base-catalyzed transesterification (homogeneous or heterogeneous), acid-catalyzed esterification and transesterification [4–7], biodiesel synthesis catalyzed by bifunctional heterogeneous solid

catalysts [8–10], enzyme-catalyzed transesterification [11–13], deoxygenation [14, 15], and supercritical methanolysis [16, 17]. In order to intensify biodiesel production, existing processes are modified in terms of treatment of reaction mixture by ultrasound [18–20] and microwave [21–23]. However, the modern concept of biodiesel production is focused on synthesis of the new catalytic systems, use of different triacylglycerol (TAG) feedstock, and improved batch and continuous reactor systems. Also, it is very important that nowadays investigations are based on the concept of low-cost production, i.e. that waste materials from various production processes are basis for catalysts, and waste feedstock as the main source of TAG.

The numerous disadvantages of homogenous base and acid catalysts, such as soap formation, catalyst recovery, high corrosion, and inhibition by water [1, 24] can be replaced using heterogeneous catalysts such as alkaline [25] and alkaline earth metal oxides [2, 26, 27], mixed oxides [28–30], modified layered double hydroxides [31–34], zeolites [35–37], sulfonated solids [38], ion exchange resins [39–41], supported heteropolyacids [42, 43], etc. In order to design new catalysts based on the modern concept of environmental protection, greatest attention of many scientists is directed at investigation of different waste materials (fly ash from coal-fired power stations (CFPSs), biomass fly ash, agricultural and animal waste, industrial waste rich in calcium such as mud and slug, and natural sources) for potential catalyst synthesis, which can often be very dangerous and leave a lasting impact on the environment. Using such materials has double benefit. The environmental and financial problems of disposal of hazardous materials can be solved, while such material can be used as a catalyst for biofuel production.

A particular challenge in the production of biofuels, primarily biodiesel, is the adaptation of the aforementioned catalytic systems in biodiesel production from waste TAG feedstock (non-edible oil, waste frying oil, and oil with high free fatty acid content), and also from TAG from sources (microalgae) related with the modern generation of biodiesel.

This review will be focused on the valorization of coal fly ash as a waste material in order to synthesize catalyst support or catalyst for biodiesel production using various modification techniques such as alkali activation, hydrothermal and thermal treatment, impregnation, and ion exchange.

2. Coal and coal fly ash: types, resources and utilization

2.1 Coal

Coal is a solid fossil fuel derived from fossilized plant matter by the process of coalification. As a geological process, over millions of years under suitable conditions (high pressure and temperature), coalification starts with dead plant matter firstly decaying into peat, and then converted into lignite, sub-bituminous, bituminous, and finally anthracite coals.

The classification into four main ranks, or types, namely lignite (lowest rank of coal), sub-bituminous, bituminous, and anthracite (highest rank of coal), is based on the content of carbon as primary coal constituent. Coal is a complex organic–inorganic system composed of mostly organic matter (non-crystalline carbon compounds) associated with petrographic maceral components, and, to a lesser extent, of inorganic matter. The inorganic constituents in coal include mineral (crystalline) matter, glassy (amorphous) matter and gas–liquid inclusions (fluid) matter [44]. The elements present in the coal are classified into three groups depending on their concentration: (1) major elements (>0.1%): C, H, O, N, S; (2) minor elements

(0.01–0.1%): Si, Al, Ca, Mg, K, Na, Fe, Mn, Ti (ash-forming elements), and occasionally Ba, Sr, P, and halogens (F, Cl, Br, I); (3) trace elements (<0.01%): As, B, Cd, Hg, Mo, Pb, which are considered hazardous pollutants [45].

Coal is the second most important fossil fuel resource for energy production, covering around 30% of global primary energy consumption [46]. The world currently consumes over 7.7 billion tons of coal which are used primarily in coal combustion processes for power generation. Bituminous, sub-bituminous and lignite are the principal energy resources in power generation with 40% of globally generated power [47]. It is reported [48] that total proved reserves at the end of 2018 were 1.055 trillion tons, enough to last about 137 years at the current rates of consumption. Nowadays, coal is simultaneously the fossil fuel with the highest carbon content (anthracite: 90–95% C, bituminous: 76–90% C, sub-bituminous: 72–76% C, lignite: 65–72% C) per unit of energy and the fossil fuel with the most abundant resources in the world.

As the most abundant low-cost energy resource, coal has various applications in many commercial processes, including power generation, iron and steel production, cement manufacturing, and production of liquid fuels. The most common and important use of coal is thermal (steam) coal utilization by pulverized coal combustion for the production of electricity and heat in CFPs. However, coal utilization technologies generate considerable amounts of greenhouse gases, primarily carbon dioxide (CO₂) due to the higher carbon content of coal, pollutants (NO_x, SO_x), and solid particulates [49]. Therefore, the utilization of thermal coal without or with reduced CO₂ emissions is a major technological challenge [50]. Accordingly, to obtain future benefits from enormous low-cost coal reserves, various efforts are necessary in order to avoid environmental risks. The promising technological solutions are clean coal technologies: cleaner and more efficient technologies for coal combustion, including supercritical coal plants, more efficient industrial boilers, fluidized bed combustion, as well as coal gasification, and various “end-of-pipe” pollution abatement technologies for CO₂ capture and storage [51].

2.2 Coal fly ash

Coal ash, an industrial solid waste, is generated from pulverized coal combustion during electricity production in CFPs. Over 70% of coal combustion residues (fly ash, bottom ash, boiler slug, and solid flue-gas desulfurization residues) contain CFA, captured by electrostatic precipitators (particulate collection equipment of flue emissions) [52], and bottom ash from the hoppers under the economizers and air preheaters of large pulverized coal boilers [53]. CFA is the most massive light-weight ash particulates, ranging from 0.5 to 300 μm dominantly spherical in shape-solid or hollow (cenospheres) [54, 55]. The major parameters affecting the characteristics of CFAs are phase-mineral and chemical composition of parent coal and coal combustion conditions in pulverized CFPs (boiler temperature and its configuration, particulate control equipment, and size of feed coal) [56]. CFAs are a complex inorganic–organic mixture (316 individual minerals and 188 mineral groups are found in coals and CFAs) and as such complicated for identification and characterization of their constituents [57]. CFAs are a complex system with the unique, multicomponent, heterogeneous and variable composition of their inorganic, organic, and fluid constituents.

The principal CFAs inorganic components (90–99%) are silicon dioxide (SiO₂) both amorphous and crystalline, aluminum oxide (Al₂O₃), ferric oxide (Fe₂O₃), and calcium oxide (CaO), the main mineral constituents of coal-bearing rock strata (coal seams) [58]. CFAs are also composed of variable amounts of some rare earth elements (Ce, Gd, La, Nd, and Sm) [59], and trace elements (e.g. As, Se, Cd, and Cr)

originating from a parent coal that make it potentially toxic [60] (Section 2.1). The bulk chemical composition and loss on ignition of CFAs (expressed as oxides) collected from various countries is shown in **Table 1**.

CFAs have a bulk chemical composition containing various metal oxides in the order: $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{CaO} > \text{Fe}_2\text{O}_3 > \text{MgO} > \text{Na}_2\text{O} > \text{K}_2\text{O} > \text{TiO}_2$ (**Table 1**). The bulk chemical composition suggests that the CFAs are aluminosilicate with higher concentration of calcium oxide than ferric oxide.

Table 2 shows the content of rare earth elements (REEs) in different countries. It is noticeable that content of some elements varies from region to region. The most abundant REEs are cerium, lanthanum, and yttrium. REEs play an important role in many areas from household products to materials used in high technologies due to their adequate properties (luminescent and magnetic). The major industries that use REEs are catalysis, metallurgy, ceramics and polishing industry. On the other hand, the wide application is focused on catalysts, high technology products, health care devices, and rechargeable batteries [55].

The content of toxic elements in CFAs is shown in **Table 3**. These elements present serious problem, causing air, soil and water pollution. From the data presented, it can be seen that in some ashes (**Table 3**) the content of some toxic element is very high. For example, the content of the arsenic in some ashes is even 0.2%. That is the exact reason such material should be utilized in order to avoid negative impact on environment and human health.

	Chemical composition and loss on ignition (%)									
	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	TiO ₂	Na ₂ O	LOI	Ref.
Australia	31.1–68.6	17–33	0.1–5.3	1–27.1	0.1–2.9	0–2	1.2–3.7	1.2–3.7	na	[56]
Bulgaria	30.1–57.4	12.5–25.4	1.5–28.9	5.1–21.2	0.8–2.8	1.1–2.9	0.6–1	0.4–1.9	0.8–32.8	[61]
Canada	35.5–62.1	12.5–23.2	1.2–13.3	3–44.7	0.5–3.2	0.4–3.1	0.4–1	0.1–7.3	0.3–9.7	[62]
China	35.6–57.2	18.8–55	1.1–7	2.3–19.3	0.8–0.9	0.7–4.8	0.2–0.7	0.6–1.3	na	[56]
Europe	28.5–59.7	12.5–35.6	0.5–28.9	2.6–21.2	0.4–4	0.6–3.8	0.5–2.6	0.1–1.9	0.8–32.8	[56]
France	47–51	26–34	2.3–3.3	6.9–9.8	na	1.5–2.2	na	2.3–6.4	0.5–4.5	[63]
Germany	20–80	1–19	2–52	1–22	0–2	0.5–11	0.1–1	0–2	0–5	[64]
India	50.2–59.7	14–32.4	0.6–9	2.7–16.6	0.2–4.7	0.1–2.3	0.3–2.7	0.2–1.2	0.5–7.2	[56]
Italy	41.7–54	25.9–33.4	2–10	3–8.8	0–2.6	0–2.4	1–2.6	0–1	1.9–9	[61]
Japan	53.9–63	18.2–26.4	2–8.1	4.2–5.7	0.6–2.7	0.9–2.4	0.8–1.2	1.1–2.1	0.5–2.1	[65]
Korea	50–55.7	24.7–28.7	2.6–6.2	3.7–7.7	1.1	0.7–1.1	na	na	4.3–4.7	[66]
Poland	32.2–53.3	4–32.2	1.2–29.9	4.5–8.9	0.2–3.3	1.2–5.9	0.6–2.2	0.2–1.5	0.5–28	[67]
Russia	40.5–48.6	23.2–25.9	6.9–13.2	na	1.9–2.6	2.6–4	0.5–0.6	1.2–1.5	na	[68]
Serbia	53.5–59.7	17.4–21	5.8–8.7	6–10.5	0.6–1.2	2–2.7	0.5–0.6	0.4–0.5	1.8–4.9	[69]
S. Africa	46.3–67	21.3–27	6.4–9.8	2.4–4.7	0.5–1	1.9–2.7	1.2–1.6	0–1.3	na	[70]
Spain	41.5–58.6	17.6–45.4	0.3–11.8	2.6–16.2	0.2–4	0.3–3.2	0.5–1.8	0–1.1	1.1–9.7	[71]
Turkey	37.9–57	20.5–24.3	0.2–27.9	4.1–10.6	0.4–3.5	1–3.2	0.6–1.5	0.1–0.6	0.4–2.7	[72]
USA	34.9–58.5	19.1–28.6	0.7–22.4	3.2–25.5	0.9–2.9	0.5–4.8	1–1.6	0.2–1.8	0.2–20.5	[56]
Min	20.0	1.0	0.1	1.0	0.0	0.0	0.1	0.0	0	
Max	80.0	55.0	52.0	44.7	4.7	11.0	3.7	7.3	32.8	

na = not available, LOI = loss on ignition—measure for unburned carbon.

Table 1.
Bulk chemical composition and loss on ignition of CFAs worldwide.

	Rare earth elements content (ppm)									
	La	Ce	Sm	Eu	Dy	Ho	Er	Y	Pr	Ref.
Austria	31.0	78.0	13.0	3.1	15.0	2.9	8.3	—	10.0	[73]
Bulgaria	37.7–40.2	82.4–87.6	7.0–7.6	1.6–1.8	5.4–5.8	1.1–1.2	2.9–3.3	30.7–35.1	9.3–9.8	[74]
Canada	25.0–95.0	43.2–173.0	4.4–14.2	1.1–4.2	3.7–19.5	1.0–2.7	2.0–7.0	—	5.1–18.1	[75]
China	79.6–81.5	191.3–195.1	17.0–17.7	3.2–3.4	13.2–13.9	2.5–2.6	7.0–7.4	64.5–66.0	21.9–23.4	[76]
Croatia	13.0	27.9	2.3	0.43	2.2	0.2	1.1	13.3	3.3	[77]
Greece	22.1	55.9	6.9	1.6	6.3	1.11	3.3	33.2	11.9	[78]
India	50–88.7	100–200	3.5–9.8	1.8–3.5	5.3–7.3	2.1–2.3	4.0–4.6	30–40	14.3–48	[59]
Japan	148	310	17.4	5.1	—	—	—	—	—	[79]
Korea	9.6–86.5	16.1–115	1.6–12.6	0.5–2.5	1.5–10.6	0.3–2.2	0.9–6.2	9.2–60.5	2.3–18.9	[80]
Poland	15.5–81.7	30.7–172.5	2.8–17.0	0.6–3.8	2.6–12.2	0.6–2.6	1.8–5.0	17.9–73.8	3.3–14.7	[65]
Russia	33.6–114.3	71.0–203.8	11.7–45.3	2.7–9.3	—	—	—	70.0–330.0	—	[81]
S. Africa	85.4	141.0	10.6	1.8	8.6	1.7	4.9	42.1	17.3	[82]
Spain	21.0–42.0	64.7–113	19.9–22.9	4.9–6.3	16.4–25.1	2.8–4.5	7.6–11.4	95.0–126.0	9.9–15.3	[83]
Turkey	36.0–41.0	72.0–85.0	6.1–7.2	1.6–1.8	5.4–5.8	1.1–1.2	2.9–3.3	30.7–35.1	9.3–9.8	[74]
USA	64.6–86.9	137–190	15.0–19.0	3.3–4.2	14.3–18.3	2.7–3.3	8.1–9.9	72.5–85.7	16.9–22.3	[84]
Min	9.6	16.1	1.7	0.4	1.5	0.2	1.1	9.2	2.3	
Max	148.0	310.0	45.3	6.3	18.3	4.5	9.9	330.0	48.0	

Table 2.
Rare earth elements content of CFAs in different countries.

	Toxic elements content (ppm)										
	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	V	Zn	Ref.
Brazil	127–1915	11–33	—	74–181	31–88	219–714	48–95	66–627	207–293	434–2453	[85]
Bulgaria	1–76	0–1	16–43	71–93	74–207	174–821	40–73	25–60	119–262	87–174	[86]
Canada	17.5–52.0	0.5–1.9	—	31–101	—	—	30–41	32–84	—	—	[87]
China	—	0–2.3	—	0–78	4–60	13–772	4–41	3–40	2.2–81.1	2.4–76.7	[88]
Croatia	—	0.1–0.9	—	14–38	28–120	—	—	2–144	11.2–624	5.73–229	[89]
EU	69	—	41	153	101	—	123	88	255	161	[90]
Greece	—	0.2–0.9	10–60	127–1502	19–227	400–1700	85–1075	4–79	49–121	12.4–35.9	[91]
India	—	—	9–18	54–103	40–83	47–182	26–63	10–56	—	29–124	[92]
Korea	0.6–25.3	0–0.4	5–19	31–119	22–73	—	16–49	12–51	—	14.4–95.0	[93]
Poland	10.2–50	0.1–2.7	—	—	13–73	—	20–72	3–101	—	11–210	[65]
Serbia	—	0–1.1	6–26	12–63	10–29	200–1270	22–1148	7–70	30–123	25–208	[94]
Slovakia	—	0.1–2.6	—	9.4–32	10–81	—	10–32	14–142	—	35–375	[95]
S. Africa	16.6	0.16	5.45	73.0	18.8	148.10	14	24	104	20.03	[96]
Spain	57–726	<0.5	22–60	167–279	72–103	225–315	89–141	54–115	225–352	53–189	[97]
Turkey	—	<5	5–13	22–252	18–141	—	30–326	2–82	—	22–270	[98]
USA	—	—	—	14–61	30–290	—	9–23	6–1600	—	163–1512	[99]
Min	0.6	0	5.0	0.25	3.9	12.8	9.0	2.0	2	2.4	
Max	1915	33	60.0	1501.8	290.0	1700.0	1075	627	624	375.0	

Table 3.
Toxic elements content of CFAs in different countries.

CFAs are commonly categorized into two chemical types for their industrial applications, by name Class C and Class F. The American Society for Testing and Materials (ASTMs) classified CFAs as Class C and Class F on the basis of chemical composition and coal origination. According to the ASTM standard C618, Class F CFA has a combined SiO_2 , Al_2O_3 , and Fe_2O_3 content of greater than 70% compared to greater than 50% for Class C CFA. Fly ash of Class F is regarded as a true pozzolanic material exhibiting cementitious properties [100]. Class C CFAs derived from lignite and sub-bituminous coals with a high CaO content of above 20% possesses self-cementitious properties. The pozzolanic (Class F CFA) and cementitious (Class C CFA) properties of CFAs may allow their use as a binding agent or as raw material to produce clinker, replacing cement in concrete manufacturing. Apart from ASTMs, the European body has devised standard EN 450-1 defining CFA as a fine powder containing mostly spherical, glassy particulates derived from burned pulverized coal, with or without co-combustion material, which has pozzolanic properties and consists essentially of SiO_2 and Al_2O_3 [56]. Vassilev and Vassileva [101] have devised a new chemical classification system in accordance to the contents of ash-forming elements in CFAs using three composition-based criteria: (1) sum of Si, Al, K, and Ti oxides; (2) sum of Ca, Mg, S, and Na oxides; (3) ferric oxide [101]. This approach resulted in four chemical CFAs types, namely sialic, calsialic, ferrisialic, and ferricalsialic. Classifying CFAs in this way should simplify the choice of utilization for each unique CFAs composition.

The abundant availability and low price of coal, rising global energy demand, and the unsteadiness of alternative energy resources launched a growth in coal-based energy use, generating large amounts of CFAs. Increase in coal production to meet the growing demand for energy has resulted in an exponential increase in the generation of CFAs from 500 in 2005 to about 750 million tons in 2015 [54, 102]. Contrarily, global use of CFA for various applications is only lower part (about 25%) of the total production while the larger part (about 75%) is disposed or stored in different ways (landfills or lagoons) depending on the processes at CFPSs, and regulations the CFPSs have to follow. CFAs are harmful if released into the environment due to the presence of metal(loid)s, toxic substances and organic pollutants [103]. The presence of toxic waste contaminants in the ash requires it to be stored appropriately. It is known that otherwise landfills can decay, causing many environmental concerns and serious troubles to local communities [104]. In the view of the imminent strict disposal restriction, the disappearing availability of landfill space and the increasing cost of disposal, demands the need for economical and green CFAs utilization technologies. Therefore, maximizing the valorization of CFA into valuable products, rather than of its storage and disposal, is the optimal solution to preserve the environment and open new economic opportunities [105]. The utilization of CFA as an industrial waste residue or by-product has received a great deal of attention over the past two decades, as more sustainable solutions to waste problems have been searched for. However, it must be emphasized that extending the CFAs utilization to various valuable products in the future, imposes the necessity of detoxifying CFA and converting extracted toxins into valuable materials to create conditions for safe conversion into new products. Contrarily, the direct utilization of CFAs leads to hazardous effects on the environment. CFAs as a pozzolanic material has been prevalently employed in manufacturing cement either as a raw material or as a supplement to save its consumption [106]. CFA has been used in different geotechnical applications such as grouting, asphalt filler, sub-grade stabilization, pavement base course, general engineering fill, structural fill, soil amendment, and infill [52]. Extensive research has been carried out for use of fly ash-based adsorbents in both gaseous and aqueous applications. CFA has been found to be effective for removing different metal ions [107, 108] and aqueous

pollutants or gaseous pollutants [58] from wastewaters. Currently, application of CFAs in wastewater treatment (WWT) is broad but still inadequate. CFAs have tremendous potential for WWT. The utilization of CFAs in water treatment in the near future is quite promising [109]. In the last few years, CFA usage as a cheap source of aluminosilicate has attracted scientists who have shown the successful transformation of this waste material into zeolites [110]. These synthetic fly ash-based zeolites are synthesized by various chemical processes (hydrothermal, alkaline fusion-assisted hydrothermal process, multi-step treatment method, microwave irradiation and sonication approach) resulting in a more uniform and cleaner state than natural types in terms of their lattice structures, pore size, and cages in their aluminosilicate frameworks [111–116].

The type of zeolites formed is a function of several reaction parameters such as temperature, pressure, the concentration of the reagent solutions, pH, process of activation and aging period, SiO_2 and Al_2O_3 contents of the CFAs. Zeolite of type A, X, Y, P, and Na-P1 are well known synthetic zeolites synthesized from CFA which have a wider range of industrial applications than their natural counterparts. The utilization of fly ash-based zeolites not only brings more revenue for CFPSs but also reduces the costs associated with the disposal of coal ashes.

The use of CFA in catalytic applications was examined for its potential to reduce the consumption of materials that have limited reserves or are expensive to produce. The application of CFA as a material to be used in heterogeneous catalysis has attracted much attention. Heterogeneous catalysis is attractive because it is often easier to recover catalysts upon completion of the reaction as compared to homogeneous catalysts. For heterogeneous catalysis, catalytic materials can be supported on other materials; their activity depends on both the active component and its interaction with the support. Typically, catalyst supports include various metal oxides such as SiO_2 , Al_2O_3 , MgO , and TiO_2 . Since the CFA consists primarily of SiO_2 and Al_2O_3 , CFAs offer desirable properties such as thermal stability for use as a support. Also, CFAs are often used as the catalytically active component.

3. CFA catalyst synthesis

In order to obtain a suitable form of CFA, it can be modified by various techniques using different synthesis conditions presented in **Table 4**.

It can be seen from the results that the main techniques, which can be used for CFA modification are alkali activation, hydrothermal and thermal treatment, wet impregnation, and ion exchange. The influence of various parameters, such as temperature, the concentration of alkali agent, the synergism of alkali agents, reaction time, aging period are crucial for obtaining the material with a suitable structure. Babajide et al. [116] studied the synthesis of Na-X zeolite from CFA, which was used as a catalyst for biodiesel production in the K-ion exchanged form. Such synthesized material exhibits higher activity than non-ion exchanged. It can be noted, that the main goal of CFA modification is the total or partial destruction of CFA crystalline cenosphere structure, with very low specific surface area and inaccessible pore system. Depending on CFA alkali activation and hydrothermal conditions (temperature, sodium-aluminate addition, and time), zeolite materials of different compositions and characteristics can be obtained. Bhandari et al. [120] optimized CFA alkali fusion process in order to obtain high crystalline zeolite and reported that zeolite with suitable structural, morphological, and textural properties can be obtained at alkali activation and hydrothermal temperature 550 °C and 90 °C, respectively and NaOH/CFA ratio of 1.5. By adding sodium aluminate in the range 10–20%, zeolite X was obtained, whereas further adding leads to the formation

Catalyst type	Catalyst synthesis		CFA and catalyst characteristics	Ref.
(A-CFA or B/CFA)	Method(s)	Conditions	Catalyst efficiency	
Sodalite (A-CFA) CFA-derived sodalite zeolite	Hydrothermal	Activators: (a) NaOH (b) NaAlO ₂ ; Aging time (AT): 6 days; Temperature (T): 100°C; Time (t): 24 h	• Diffraction peaks: quartz (SiO ₂), mullite (3Al ₂ O ₃ ·2SiO ₂), small amounts muscovite and sodalite (Na ₈ Al ₆ Si ₆ O ₂₄ Cl ₂) (XRD); rounded particles of sodalite agglomerates (SEM); mesoporous sodalite: N ₂ ads/des type IV isotherm; S _{BET} : 9.7 m ² /g	[117]
	High potential of zeolite sodalite as a low-price product to be used as a catalyst for biodiesel production on an industrial scale.		Soybean oil transesterification: Catalyst loading/FAME • 4 wt%/95.5 wt% FAME	
Eggshell/CFA (B/CFA) CaO/CFA catalyst Impregnated CFA-based catalyst	Drying starting material	(a) Eggshell T: 105°C; t: 24 h (b) Fly ash T: 100 ± 5°C; t: 24 h	• Crystalline: α-quartz, hematite, mullite, calcium oxide (CaO), dicalcium silicate (Ca ₂ SiO ₄) (XRD); agglomerated structures of calcined metal oxides (SEM); mesoporous solid: N ₂ ads/des type III isotherm; S _{BET} : 0.7 m ² /g	[118]
	Impregnation (wet)	T: 70°C; t: 4 h; pH: 12.10; AT: 24 h		
	Calcination	T: 1000°C; t: 2 h		
Effective waste valorization is procreated through the preparation of a novel low-cost catalyst for synthesis of fuel-grade biodiesel.			Soybean oil transesterification: Catalyst loading/FAME • 1.0 wt%/96.97 wt% FAME	
Modified^{MW} CFA (A-CFA) MW modified	Alkali fusion	CFA:NaOH = 1:1.5; T: 600°C; t: 1.5 h;	Microwave irradiation (MW) • Amorphous glassy phase (untreated CFA), SiO ₂ and mullite (calcined CFA), new crystal phases NaAlO ₂ , Na ₂ SiO ₃ upon MW (XRD); OH- and SO ₄ ²⁻ supported on CFA upon MW (FTIR)	[23]
	Hydrothermal	30 wt% Na ₂ SO ₄ ; T: 60°C; t: 10 h		
	Microwave (MW)			
	Calcination	T: 600°C; t: 1.5 h		
Modified coal fly ash catalyst improved biodiesel yields under the microwave irradiation system.			Waste cooking oil transesterification: Catalyst loading/FAME 3.99 wt%/94.91 wt% FAME	
Modified^{US} CFA (A-CFA) US modified	Alkali fusion	CFA:KOH = 1:1; T: 550°C; t: 2 h;	Ultrasound-assisted (US) • Amorphous glassy phase (untreated CFA), SiO ₂ and Al ₆ Si ₂ O ₁₃ (calcined CFA), new crystal phases KAlO ₂ , K ₂ SiO ₃ upon US (XRD); OH- and NO ₃ ⁻ supported on CFA upon ultrasound-assisted (FTIR)	[119]
	Hydrothermal	30 wt% KNO ₃ ; T: 100°C; t: 6 h		
	Ultrasound (US)			
	Calcination	T: 550°C; t: 2 h		
Experimental results showed that the modified coal fly ash catalyst could improve biodiesel yields under ultrasound assisting system.			Waste cooking oil transesterification: Catalyst loading/FAME • 4.97 wt%/95.57 wt% FAME	
KX-CFA (A-CFA) CFA-derived zeolite KX	CFA calcination	T: 850°C; t: 2 h	• Diffraction peaks: crystalline quartz and mullite (XRD); spherical CFA particles, CFA, octahedral crystals ion exchanged zeolite KX (FESEM); mesoporous zeolitic material: N ₂ ads/des type II isotherm; S _{BET} : 735.8 m ² /g	[120]
	CFA acidification	HCl; T: 80°C; t: 1.5 h;		
	Alkali fusion	NaOH:CFA = 1:1–1:2; T: 400–600°C; t: 1 h;		
	Hydrothermal	T: 90–120°C; t: 4–24 h		

Catalyst type	Catalyst synthesis		CFA and catalyst characteristics	Ref.
(A-CFA or B/CFA)	Method(s)	Conditions	Catalyst efficiency	
	Ion exchange	1.0 M CH ₃ COOK		
	Calcination	T: 500 °C; t: 2 h		
The effective utilization of fly ash for zeolite KX synthesis and its use as a catalyst for transesterification would improve ecological balance and helps in value addition.			Soybean oil transesterification: Catalyst loading/FAME • 3.0 wt%/81.2 wt% FAME	
Animal bone/CFA (B/CFA) Impregnated CFA-based catalyst	CFA drying	T: 105°C; t: overnight;	• CFA chemical composition (wt%): [121] 56.6 SiO ₂ , 23.2 Al ₂ O ₃ , 5.8 Fe ₂ O ₃ , and 7.9 CaO (AAS); overall crystalline phases: quartz, mullite (CFA), dicalcium silicate (Ca ₂ SiO ₄), hydroxyapatite (Ca ₅ (PO ₄) ₃ OH), β-tricalcium phosphate, and CaO (XRD); surface morphology: cenospheres (CFA), rod like crystalline particles (impregnated fly ash catalysts C10, C20, and C30) (SEM); basicity: 5.1–17.4 mmoles HCl/g; mesoporous solids: N ₂ ads/des type III isotherm; S _{BET} (m ² /g): 1.7 CFA, 100 CABP, 11.3 C10, 7.1 C20, 4.2 C30	
	Animal bones calcination	T: 900°C; t: 2 h;		
	Impregnation (wet)	T: 70°C; t: 4 h; L: S = 10: 1; pH:12.1; AT: 24 h		
	Calcination	T: 900°C; t: 2 h		
Animal bones (calcium enriched waste materials) impregnated in fly ash might be a potential source of catalyst in biodiesel production.			Mustard oil transesterification: Catalyst loading/FAME • 10 wt%/90.4 wt% FAME	
Kaliophilite (A-CFA) CFA-derived kaliophilite catalyst	Geopolymer synthesis	Alkali activator (KOH in potassium water glass); T: 80°C; t: 24 h	• Amorphous aluminosilicate, quartz and mullite crystals (CFBFA), amorphous geopolymer, and KAlSiO ₄ (as-synthesized kaliophilite catalyst) (XRD); irregular CFBFA particles (30 μm), dense structure (geopolymer), prismatic crystals (~1 μm) (kaliophilite) (SEM); medium-strength basic sites (K-O ion pairs) and high strength basic sites (surface O ²⁻ ion) (TPD-CO ₂); mesoporous catalyst: N ₂ ads/des type IV isotherm; S _{BET} : 3.49 (m ² /g)	[122]
	Hydrothermal	Geopolymer monolith:50 ml KOH; T: 180°C; t: 24 h		
	Drying kaliophilite	T: 105°C; t: 12 h		
Circulating fluidized bed fly ash (CFBFA) was used to synthesize kaliophilite catalyst via a facile and low-energy two-step process: fabrication of amorphous CFBFA geopolymer and hydrothermal transformation of CFBFA based geopolymer into kaliophilite. This catalyst affords three benefits: high value-added reutilization of CFBFA industrial by-products, low-energy synthesis of kaliophilite, and low-cost production of biodiesel.			Canola oil transesterification: Catalyst loading/FAME • 5.0 wt%/99.2 wt% FAME	
FA/Na-X (A-CFA) FA-derived zeolite Na-X	Hydrothermal	—	• Low Si/Al ratio preferentially result in zeolite FA/Na-X (XRD); faujasite phase irregular crystals (unique morphology) (SEM); S _{BET} (m ² /g): 320 (FA/Na-X), 257 (FA/Na-X)	[116]
	Ion exchange	L:S = 10:1; 1.0 M CH ₃ COOK; T: 60–70°C; t: 24 h		
	Calcination	T: 500 °C; t: 2 h		
Fly ash transformed into a zeolite Na-X phase and exchanged with K proved to be suitable for use as a catalyst in biodiesel synthesis under less rigorous conditions.			Sunflower oil transesterification: Catalyst loading (FA/K-X)/FAME • 3 wt%/85.5 wt% FAME	

Catalyst type	Catalyst synthesis		CFA and catalyst characteristics	Ref.
(A-CFA or B/CFA)	Method(s)	Conditions	Catalyst efficiency	
KNO₃/CFA (B/CFA) Impregnated CFA-based catalyst	Impregnation (wet)	KNO ₃ aq. stock; solution; L:S = 1:1; KNO ₃ :FA = 1:1	• Crystalline phases: α-quartz, hematite, mullite (CFA), KNO ₃ (KNO ₃ /CFA catalyst) surface morphology: cenospheres (CFA), potassium impregnated fly ash spherical particles aggregates (>10 μm) (SEM); N ₂ ads/des type III isotherm; S _{BET} : 0.55 (m ² /g)	[123, 124]
	Calcination	T: 500–700°C; t: 5 h		
Fly ash loaded with KNO ₃ was used as a solid base catalyst in the transesterification of sunflower oil to methyl esters to make a meaningful utilization of fly ash.			Sunflower oil transesterification: Catalyst loading/FAME • 5 wt%/87.5 wt% FAME	
K-Zeolite (A-CFA) CFA-derived K-Zeolite	CFA drying	T: 80°C; t: overnight;	• Main crystalline phases: hexagonal quartz (SiO ₂), orthorhombic mullite crystalline phase (3Al ₂ O ₃ ·2SiO ₂) (CFA), K-Zeolite ≡ K-CHA zeolite (potassium type zeolite) (hydrothermally activated XRD pattern); prism-like crystals zeolite crystals (SEM micrographs); mesoporous solids: N ₂ ads/des type IV isotherm; S _{BET} (m ² /g): 2.1 coal fly ash, 24.7 K-Zeolite	[125]
	CFA calcination	T: 900°C; t: 3 h;		
	Hydrothermal	5 M KOH (aq. stock solution); CFA:KOH = 1:4; T: 160°C; t: 8 h		
	Drying product	T: 80°C; t: overnight		
	Calcination	T: 450°C; t: 4 h		
The obtained K-Zeolite can be used in biodiesel industry. Utilization of biodiesel by-product glycerol is of great importance for sustainability of biodiesel industry. Conversion of glycerol to value-added chemicals increases the profitability of biodiesel production.			Glycerol transesterification: Catalyst loading/Glycerol carbonate • 4 wt%/96.0 wt% Glycerol carbonate	
CaO/Fly ash (B/CFA) CaO/Fly ash catalyst Impregnated Fly ash-based catalyst	Starting material	(a) 50 wt% Fly ash (b) 50 wt% Ca (NO) ₃ · 4H ₂ O Ca(NO) ₃ ·4H ₂ O = CaO _p	• Crystalline phases: quartz (SiO ₂), calcium oxide (CaO), dicalcium silicate (Ca ₂ SiO ₄), and calcium hydroxide Ca(OH) ₂ (XRD); basicity: H ₊ < 8.2 (FA), H ₊ > 9.3 (C1, C2 and C3); S _{BET} (m ² /g): 24.3 C2 (800°C), 909.8 C2 (850°C)	[126]
	Impregnation (wet)	—		
	Calcination	T: 800, 850 and 900°C		
	CaO/FA catalyst	CaO _p :FA = 70:30 (C1); CaO _p :FA = 80:20 (C2); CaO _p :FA = 90:10 (C3)		
Palm fly ash supported calcium oxide (CaO) catalyst was prepared through impregnation method and used in transesterification from off-grade palm oil for biodiesel manufacturing. The efficiency of CaO/Fly ash is affected by its basic strength.			Palm oil transesterification: Catalyst loading/FAME • 6 wt%/71.77 wt% FAME	
CFA-HT (A-CFA) FA-hydrotalcite catalyst	Alkali fusion	FZ	• XRD patterns consistent with hydrotalcite materials; basicity (mmoles HCl/g): 36.6 FZ-HT, 28.8 C-HT and 12.4 F-HT; surface morphology: cenospheres (Fly ash), octahedral crystals (FZ), platelet-like morphology (C-HT), platelet-like structures of HT (F-HT and FZ-HT); mesoporous solids: N ₂ ads/	[127]
	Hydrothermal			
	Coprecipitation	C-HT		
		F-HT		
		FZ-HT		
Calcination	T: 500 °C; t: 6 h			

Catalyst type	Catalyst synthesis		CFA and catalyst characteristics	Ref.
(A-CFA or B/CFA)	Method(s)	Conditions	Catalyst efficiency	
			des type III isotherm (Fly ash), type II isotherm (FZ), type IV isotherm (F-HT), type IV isotherm (FZ-HT); S_{BET} (m^2/g): 1.7 Fly ash, 323.2 FZ, 32.9 C-HT, 39.6 F-HT, and 476.6 FZ-HT	
Mg-Al hydrotalcite-like catalysts were prepared from fly ash and fly ash-based zeolite by coprecipitation method. The activity of prepared catalyst was estimated in mustard oil transesterification. The FAME yield tends to increase with increasing BET surface area.			Mustard oil transesterification: Catalyst loading/FAME • 7 wt%/93.4 wt% FAME	
A. granosa and P. undulata/CFA (B/CFA) CaO/CFA catalyst Impregnated CFA-based catalyst	Drying starting material	(a) Shells T: 110°C; t: 6 h (b) Fly ash T: 105°C; t: 10 h	• Identified phases: SiO ₂ (crystalline phase), Al ₂ O ₃ amorphous phase (Fly ash), Ca ₂ SiO ₄ dicalcium silicate (calcined impregnated catalyst) (XRD); smaller morphology size of particles: <i>P. undulata</i> shell less than 75 μm , <i>A. granosa</i> shell less than 85 μm , fly ash supported CaO catalyst had the size less than 30 μm	[128]
	Impregnation (wet)	—		
	Calcination	T: 800°C; t: 3 h		
Fly ash supported CaO catalyst derived from waste mollusk shell of <i>Anadara granosa</i> and <i>Paphia undulata</i> was used for palm oil transesterification. This catalyst could gain the yield of FAME of 92 and 94 wt% for <i>A. granosa</i> and <i>P. undulata</i> shell, respectively.			Palm oil transesterification: Catalyst loading/FAME • 6 wt%/94.0 wt% FAME	
Sulfated fly ash (SFA) (A-CFA) SFA-sulfated fly ash catalyst	Sulfonation	—	• Crystalline phases: quartz, mullite, hematite, lime; thermally stable up to 550°C; acid sites: 0.401 mmol/g (NH ₃ -TPD), basic sites: 0.197 mmol/g (CO ₂ -TPD); SO ₄ ²⁻ groups is confirmed by FTIR analysis; surface morphology: homogeneous distribution of small spherical pores on FA surface, large connected spherical pores on SFA catalyst surface; SFA crystallite size: 16.8 nm; S_{BET} (m^2/g): 38.3	[129]
The goal is on the fly ash utilization for the development of sulfated fly ash (SFA) catalyst synthesis under solvent-free conditions. The use of SFA catalyst has been found to be advantageous in biodiesel synthesis from feedstock with high free fatty acids content.			Maize acid oil esterification: Catalyst loading/FAME • 5 wt%/98.3 wt% FAME	
CFA-Zeolite X (A-CFA) CFA-derived Zeolite X	Alkali fusion	T: 450–600°C; t: 1–2 h; CFA:NaON = 1:1–1:2.5	• Identified crystalline phases: Pure single-phase zeolites X and A under following conditions: FA: NaOH = 1:1.2, crystallization time 1 h (Zeolite X), 12 h (Zeolite A), fusion temperature 550°C, crystallization temperature 110°C, and calcination temperature 800°C; cations exchange Zeolite A (highest value); S_{BET} (m^2/g): 167.4 (Zeolite X), 24.1 (Zeolite A)	[130]
	Hydrothermal	10–30 wt% NaAlO ₂ ; L:S = 10:1; T: 90–120°C; t: 24 h; AT = 12–16 h		
	Ion exchange	1 M CH ₃ COOK; L:S = 10:1; T: 60°C; t: 24 h		
	Calcination	T: 500 °C; t: 2 h		

Catalyst type	Catalyst synthesis		CFA and catalyst characteristics	Ref.
(A-CFA or B/CFA)	Method(s)	Conditions	Catalyst efficiency	
	Different types of single-phase zeolites (Zeolite X and Zeolite A) with high cations exchange capacity were synthesized from alkali fusion followed by hydrothermal treatment of coal fly ash as source material. Coal fly ash was used successfully for production of biodiesel in mustard oil transesterification with suitable calorific value (37.5 MJ/kg).		Mustard oil transesterification: Catalyst loading/FAME • 5 wt%/84.6 wt% FAME	

Table 4.
Synthesis of CFA based heterogeneous catalyst for biodiesel production.

of zeolite A. In this study, the K-exchanged form of zeolite X exhibits suitable catalytic properties during the production of biodiesel from soybean oil. From previous and similar investigations, it is obvious, that the activity of the zeolite-based catalyst can be improved by impregnation of mainly alkaline metals, such as potassium. The content of some alkali metals (Na and K) in biodiesel fuel is regulated by EN 14214, (max. concentration 5 ppm). Due to high leaching affinity, such catalysts are unsuitable. In order to obtain an active and stable catalytic form, previously treated CFA can be modified with different CaO-based active catalytic components. Volli et al. [121] investigated the utilization of CFA by impregnation of calcium from animal bones in order to synthesize catalysts for biodiesel production from mustard oil. The highest catalytic activity (TAG conversion of 90.4%) is achieved by catalyst with 10 wt% loaded animals bones powder on CFA. However, further increasing of animal bone powder loading on CFA leads to decreasing of catalytic activity. Waste materials such as eggshells are efficient as a high calcium source, which can be used as biodiesel catalysts. Carbonate eggshell form can be converted into active oxide form using simple synthesis methods (thermal activation and modification techniques).

4. Biodiesel synthesis over CFA based catalyst

In recent years, most studies have shown that CFA can successfully catalyze transesterification of various oily feedstock in order to produce biodiesel. Pure CFA is practically inactive, but in the modified form it could exhibit high catalytic activity. In **Table 5** are shown different catalysts and their catalytic performance for biodiesel production from various feedstock. Xiang et al. [122] investigated alkali activated CFA modified by sodium sulfate under hydrothermal conditions, whereby transesterification reaction was carried out under microwave [23] and ultrasound [122] conditions. The high catalytic activity was achieved for short reaction time and it was shown that catalyst could be used even eight times without any loss of catalytic activity. Other modification methods are based on CFA conversion into zeolite or hydrotalcite, impregnation of alkali or alkali earth metals or ion exchange of previously mentioned zeolites.

CaO from chicken eggshell supported on CFA exhibits the highest catalytic activity (97.0%) and stability (16 reaction cycles) in the transesterification reaction. Volli et al. [124] prepared CaO from animal bones supported on fly ash and tested in biodiesel production. The satisfactory conversion (90.4%) was achieved after 6 h, whereas the catalyst suffered negligible loss of activity when tested for 5 cycles of reuse. On the other hand, Bhandari et al. [120] and Volli and Purkait [130] used potassium ion exchanged fly ash zeolite for biodiesel production, where the prepared catalyst gave yield of 81.2% and conversion of 84.6% for 8 and 7 h,

Catalyst	Feedstock	Reaction condition				C or Y	RC	Refs.
		T	MOR	CC	t			
Modified ^{MW} CFA	WCO	66.2	9.67	3.99	0.1	94.9 (C)	8	[23]
Modified ^{US} CFA	WCO	—	10.71	4.97	0.03	95.6 (C)	8	[119]
KX-CFA	Soybean oil	65	6	3	8	81.2 (C)	—	[120]
Eggshell/CFA	Soybean oil	70	6.9	1	5	97.0 (C)	16	[118]
Animal bone/CFA	Mustard oil	65	5.5	10	6	90.4 (C)	5	[121]
Sodalite	Soybean oil	65	12	4	2	95.5 (C)	—	[117]
Kaliophilite	Canola oil	85	15	5	6	99.2 (C)	4	[122]
FA/Na-X	Sunflower oil	65	6	3	8	83.5 (Y)	3	[116]
KNO ₃ /CFA	Sunflower oil	160	15	15	5	86.1 (C)	—	[123]
KNO ₃ /CFA	Sunflower oil	120	15	5	8	81.5 (C)	1	[124]
K-Zeolite	Glycerol	75	3	4	1.5	90.2 (C)	5	[125]
CaO/Fly ash	Palm oil	70	6	6	3	71.7 (C)	—	[126]
CFA-HT	Mustard oil	65	12	7	6	93.4 (Y)	—	[127]
<i>A. granosa</i> /CFA	Palm oil					92.0 (Y)	3	[128]
<i>P. undulata</i> /CFA	Palm oil					94.0 (Y)		[128]
Sulfated fly ash (SFA)	Maize acid oil	125	15	5	3	98.3 (C)	3	[129]
CFA-Zeolite X	Mustard oil	65	12	5	7	84.6 (C)	3	[130]

T = reaction temperature (°C), *MOR* = methanol/oil molar ratio, *CC* = catalyst concentration (wt%), *t* = reaction time (h), *C* or *Y* = conversion or yield (%), *RC* = reaction cycle, *WCO* = waste cooking oil.

Table 5.
Biodiesel synthesis over CFA based catalysts.

respectively. Except for zeolites, active catalytic form or adequate catalytic support can be achieved by conversion of CFA into layered double hydroxides known as hydrotalcites [127]. High biodiesel yield can be obtained by using such materials under mild conditions. Lathiya et al. [129] synthesized a sulfated fly ash catalyst, which exhibits high catalytic activity, but in comparison with other presented catalytic systems, such activity can be achieved under more rigorous conditions, which is a feature of acid heterogeneously catalyzed biodiesel production.

5. Conclusion

This review reports a brief overview of the developments of various heterogeneous catalysts derived from industrial and biological waste materials as an efficient solid base catalyst for biodiesel production. As one of the few renewable energy fuel cost-effective options that can be recycled, low-cost biodiesel generation brings with it economic as well as social and environmental benefits. The fundamentals of methanolysis, the role of various process parameters and factors affecting biodiesel production from different feedstock are highlighted to guide future research and development on this topic. The development of heterogeneous fly ash-based catalysts supported with alkaline and alkaline earth metal (oxides, hydroxides, salts) gained a great awareness due to the wide availability of alkaline/alkaline earth metal-rich waste materials and their corresponding high catalytic activity in the methanolysis of triacylglycerol oils.

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References

- [1] Marinković D, Stanković M, Veličković A, Avramović J, Miladinović M, Stamenković O, et al. Calcium oxide as a promising heterogeneous catalyst for biodiesel production: Current state and perspectives. *Renewable and Sustainable Energy Reviews*. 2016;**56**: 1387-1408. DOI: 10.1016/j.rser.2015.12.007
- [2] Marinković D, Avramović A, Stanković M, Stamenković O, Jovanović D, Veljković V. Synthesis and characterization of spherically-shaped $\text{CaO}/\gamma\text{-Al}_2\text{O}_3$ catalyst and its application in biodiesel production. *Energy Conversion and Management*. 2017;**144**: 399-413. DOI: 10.1016/j.enconman.2017.04.079
- [3] Shan R, Lu L, Shi Y, Yuan H, Shi J. Catalysts from renewable resources for biodiesel production. *Energy Conversion and Management*. 2018;**178**: 277-289. DOI: 10.1016/j.enconman.2018.10.032
- [4] Gebremariam SN, Marchetti JM. Biodiesel production through sulfuric acid catalyzed transesterification of acidic oil: Techno economic feasibility of different process alternatives. *Energy Conversion and Management*. 2018;**174**: 639-648. DOI: 10.1016/j.enconman.2018.08.078
- [5] Wang YT, Fang Z, Zhang F. Esterification of oleic acid to biodiesel catalyzed by a highly acidic carbonaceous catalyst. *Catalysis Today*. 2019;**319**:172-181. DOI: 10.1016/j.cattod.2018.06.041
- [6] Lu W, Alam MA, Wu C, Wang Z, Wei H. Enhanced deacidification of acidic oil catalyzed by sulfonated granular activated carbon using microwave irradiation for biodiesel production. *Chemical Engineering and Processing Process Intensification*. 2019;**135**:168-174. DOI: 10.1016/j.cep.2018.10.019
- [7] Wang YT, Fang Z, Yang XX, Yang YT, Luo J, Xu K, et al. One-step production of biodiesel from Jatropha oils with high acid value at low temperature by magnetic acid-base amphoteric nanoparticles. *Chemical Engineering Journal*. 2018;**348**:929-939. DOI: 10.1016/j.cej.2018.05.039
- [8] Jeon Y, Chi WS, Hwang J, Kim DH, Kim JH, Shul YG. Core-shell nanostructured heteropoly acid-functionalized metal-organic frameworks: Bifunctional heterogeneous catalyst for efficient biodiesel production. *Applied Catalysis B: Environmental*. 2019;**242**:51-59. DOI: 10.1016/j.apcatb.2018.09.071
- [9] Farooq M, Ramli A, Subbarao D. Biodiesel production from waste cooking oil using bifunctional heterogeneous solid catalysts. *Journal of Cleaner Production*. 2013;**59**:131-140. DOI: 10.1016/j.jclepro.2013.06.015
- [10] Mansir N, Teo SH, Rashid U, Saiman MI, Tan YP, Alsultan GA, et al. Modified waste egg shell derived bifunctional catalyst for biodiesel production from high FFA waste cooking oil. A review. *Renewable and Sustainable Energy Reviews*. 2018;**82**:3645-3655. DOI: 10.1016/j.rser.2017.10.098
- [11] Andrade TA, Martín M, Errico M, Christensen KV. Biodiesel production catalyzed by liquid and immobilized enzymes: Optimization and economic analysis. *Chemical Engineering Research and Design*. 2019;**141**:1-14. DOI: 10.1016/j.cherd.2018.10.026
- [12] Adewale P, Vithanage LN, Christopher L. Optimization of enzyme-catalyzed biodiesel production from crude tall oil using Taguchi method. *Energy Conversion and Management*.

- 2017;**154**:81-91. DOI: 10.1016/j.enconman.2017.10.045
- [13] Guldhe A, Singh B, Mutanda T, Permaul K, Bux F. Advances in synthesis of biodiesel via enzyme catalysis: Novel and sustainable approaches. *Renewable and Sustainable Energy Reviews*. 2015;**41**:1447-1464. DOI: 10.1016/j.rser.2014.09.035
- [14] Jeon KW, Shim JO, Cho JW, Jang WJ, Na HS, Kim HM, et al. Synthesis and characterization of Pt-, Pd-, and Ru-promoted Ni-Ce_{0.6}Zr_{0.4}O₂ catalysts for efficient biodiesel production by deoxygenation of oleic acid. *Fuel*. 2019;**236**:928-936. DOI: 10.1016/j.fuel.2018.09.078
- [15] Viêgas CV, Hachemi I, Freitas SP, Arvela PM, Aho A, Hemming J, et al. A route to produce renewable diesel from algae: Synthesis and characterization of biodiesel via in situ transesterification of *Chlorella alga* and its catalytic deoxygenation to renewable diesel. *Fuel*. 2015;**155**:144-154. DOI: 10.1016/j.fuel.2015.03.064
- [16] Farobie O, Leow ZYM, Samanmulya T, Matsumura Y. New insights in biodiesel production using supercritical 1-propanol. *Energy Conversion and Management*. 2016;**124**: 212-218. DOI: 10.1016/j.enconman.2016.07.021
- [17] Aboelazayem O, Gadalla M, Saha B. Valorisation of high acid value waste cooking oil into biodiesel using supercritical methanolysis: Experimental assessment and statistical optimisation on typical Egyptian feedstock. *Energy*. 2018;**162**:408-420. DOI: 10.1016/j.energy.2018.07.194
- [18] Korkut I, Bayramoglu M. Selection of catalyst and reaction conditions for ultrasound assisted biodiesel production from canola oil. *Renewable Energy*. 2018;**116**:543-551. DOI: 10.1016/j.renene.2017.10.010
- [19] Korkut I, Bayramoglu M. Ultrasound assisted biodiesel production in presence of dolomite catalyst. *Fuel*. 2016;**180**:624-629. DOI: 10.1016/j.fuel.2016.04.101
- [20] Tan SX, Lim S, Ong HC, Pang YL. State of the art review on development of ultrasound-assisted catalytic transesterification process for biodiesel production. *Fuel*. 2019;**235**:886-907. DOI: 10.1016/j.fuel.2018.08.021
- [21] Jin LJ, Wen CY. Production of biodiesel by transesterification of Jatropha oil with microwave heating. *Journal of the Taiwan Institute of Chemical Engineers*. 2017;**75**:43-50. DOI: 10.1016/j.jtice.2017.03.034
- [22] Hong IK, Jeon H, Kim H, Lee SB. Preparation of waste cooking oil based biodiesel using microwave irradiation energy. *Journal of Industrial and Engineering Chemistry*. 2016;**42**: 107-112. DOI: 10.1016/j.jiec.2016.07.035
- [23] Xiang Y, Xiang Y, Wang L. Microwave radiation improves biodiesel yields from waste cooking oil in the presence of modified coal fly ash. *Journal of Taibah University of Science*. 2017;**11**:1019-1029. DOI: 10.1016/j.jtusc.2017.05.006
- [24] Lam MK, Lee KT, Mohamed AR. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. *Biotechnology Advances*. 2010;**28**:500-518. DOI: 10.1016/j.biotechadv.2010.03.002
- [25] Hindryawati N, Maniam GP, Karim MR, Chong KF. Transesterification of used cooking oil over alkali metal (Li, Na, K) supported rice husk silica as potential solid base catalyst. *Engineering Science and Technology, an International Journal*. 2014;**17**:95-103. DOI: 10.1016/j.jestch.2014.04.002

- [26] Su M, Yang R, Li M. Biodiesel production from hempseed oil using alkaline earth metal oxides supporting copper oxide as bi-functional catalysts for transesterification and selective hydrogenation. *Fuel*. 2013;**103**:398-407. DOI: 10.1016/j.fuel.2012.07.009
- [27] Arzamendi G, Arguiñarena E, Campo I, Zabala S, Gandía LM. Alkaline and alkaline-earth metals compounds as catalysts for the methanolysis of sunflower oil. *Catalysis Today*. 2008;**1**: 305-315. DOI: 10.1016/j.cattod.2007.11.029
- [28] Salinas D, Sepúlveda C, Escalona N, Fierro JLG, Pecch G. Sol-gel $\text{La}_2\text{O}_3\text{-ZrO}_2$ mixed oxide catalysts for biodiesel production. *Journal of Energy Chemistry*. 2018;**27**:562-572. DOI: 10.1016/j.jechem.2017.11.003
- [29] Guldhe A, Moura VRC, Singh P, Rawat I, Moura ME, Sharma Y, et al. Conversion of microalgal lipids to biodiesel using chromium-aluminum mixed oxide as a heterogeneous solid acid catalyst. *Renewable Energy*. 2017; **105**:175-182. DOI: 10.1016/j.renene.2016.12.053
- [30] Fan M, Liu Y, Zhang P, Jiang P. Blocky shapes Ca-Mg mixed oxides as a water-resistant catalyst for effective synthesis of biodiesel by transesterification. *Fuel Processing Technology*. 2016;**149**:163-168. DOI: 10.1016/j.fuproc.2016.03.029
- [31] Navajas A, Campo I, Moral A, Echave J, Sanz O, Montes M, et al. Outstanding performance of rehydrated Mg-Al hydrotalcites as heterogeneous methanolysis catalysts for the synthesis of biodiesel. *Fuel*. 2018;**211**:173-181. DOI: 10.1016/j.fuel.2017.09.061
- [32] Dias APS, Bernardo J, Felizardo P, Correia MJN. Biodiesel production over thermal activated cerium modified Mg-Al hydrotalcites. *Energy*. 2012;**41**:344-353. DOI: 10.1016/j.energy.2012.03.005
- [33] Navajas A, Campo I, Arzamendi G, Hernández WY, Bobadilla LF, Centeno MA, et al. Synthesis of biodiesel from the methanolysis of sunflower oil using PURAL® Mg-Al hydrotalcites as catalyst precursors. *Applied Catalysis B: Environmental*. 2010;**100**:299-309. DOI: 10.1016/j.apcatb.2010.08.006
- [34] Reyero I, Velasco I, Sanz O, Montes M, Arzamendi G, Gandía LM. Structured catalysts based on Mg-Al hydrotalcite for the synthesis of biodiesel. *Catalysis Today*. 2013;**216**: 211-219. DOI: 10.1016/j.cattod.2013.04.022
- [35] Alismaeel ZT, Abbas AS, Albayati TM, Doyle AM. Biodiesel from batch and continuous oleic acid esterification using zeolite catalysts. *Fuel*. 2018;**234**:170-176. DOI: 10.1016/j.fuel.2018.07.025
- [36] Jammal NA, Hamamre ZA, Alnaief M. Manufacturing of zeolite based catalyst from zeolite tuft for biodiesel production from waste sunflower oil. *Renewable Energy*. 2016; **93**:449-459. DOI: 10.1016/j.renene.2016.03.018
- [37] Wang YY, Chen BH. High-silica zeolite beta as a heterogeneous catalyst in transesterification of triolein for biodiesel production. *Catalysis Today*. 2016;**278**:335-343. DOI: 10.1016/j.cattod.2016.03.012
- [38] Wang T, Xu Y, He Z, Zhou M, Yu W, Shi B, et al. Fabrication of sulphonated hollow porous nanospheres and their remarkably improved catalytic performance for biodiesel synthesis. *Reactive and Functional Polymers*. 2018;**132**:98-103. DOI: 10.1016/j.reactfunctpolym.2018.09.014
- [39] Jaya N, Selvan BK, Vennison SJ. Synthesis of biodiesel from pongamia oil using heterogeneous ion-exchange resin catalyst. *Ecotoxicology and*

- Environmental Safety. 2015;**121**:3-9. DOI: 10.1016/j.ecoenv.2015.07.035
- [40] Kitakawa NS, Kitakawa NS, Ihara T, Nakashima K, Yonemoto T. Production of high quality biodiesel from waste acid oil obtained during edible oil refining using ion-exchange resin catalysts. *Fuel*. 2015;**139**:11-17. DOI: 10.1016/j.fuel.2014.08.024
- [41] Deboni TM, Hirata GAM, Shimamoto GG, Tubino M, Meirelles AJA. Deacidification and ethyl biodiesel production from acid soybean oil using a strong anion exchange resin. *Chemical Engineering Journal*. 2018;**333**: 686-696. DOI: 10.1016/j.cej.2017.09.107
- [42] Monge JA, Bakkali BE, Trautwein G, Reinoso S. Zirconia-supported tungstophosphoric heteropolyacid as heterogeneous acid catalyst for biodiesel production. *Applied Catalysis B: Environmental*. 2018;**224**:194-203. DOI: 10.1016/j.apcatb.2017.10.066
- [43] Xiang HX, Ke CK, Wei Y, Liu HC, Li L, Hao WP, et al. Amino acid-functionalized heteropolyacids as efficient and recyclable catalysts for esterification of palmitic acid to biodiesel. *Fuel*. 2016;**165**:115-122. DOI: 10.1016/j.fuel.2015.10.027
- [44] Vassilev SV, Tascón JMD. Methods for characterization of inorganic and mineral matter in coal: A critical overview. *Energy & Fuels*. 2003;**17**: 271-281. DOI: 10.1021/ef020113z
- [45] Vejehati F, Xu Z, Gupta R. Trace elements in coal: Associations with coal and minerals and their behavior during coal utilization—A review. *Fuel*. 2010; **89**:904-911. DOI: 10.1016/j.fuel.2009.06.013
- [46] World Energy Council (WEC). World Energy Resources Report [Internet]. 2016. Available from: <https://www.worldenergy.org/assets/images/imported/2016/10/World-Energy-Resources-Full-report-2016.10.03.pdf> [Accessed: 04 August 2019]
- [47] Melikogly M. Clean coal technologies: A global to local review for Turkey. *Energy Strategy Reviews*. 2018; **22**:313-319. DOI: 10.1016/j.esr.2018.10.011
- [48] BP Statistical Review of World Energy/68th edition [Internet]. 2019. Available from: <https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2019-coal.pdf> [Accessed: 08 August 2019]
- [49] IEA. Clean Coal Centre (CCC TCP) [Internet]. 2017. Available from: <https://www.iea.org/tcp/fossilfuels/ccc/> [Accessed: 29 September 2019]
- [50] Tang X, Snowden S, McLellan BC, Höök M. Clean coal use in China: Challenges and policy implications. *Energy Policy*. 2015;**87**:517-523. DOI: 10.1016/j.enpol.2015.09.041
- [51] Mishra MK, Khare N, Agrawal AB. Scenario analysis of the CO₂ emissions reduction potential through clean coal technology in India's power sector: 2014–2050. *Energy Strategy Reviews*. 2015;**7**: 29-38. DOI: 10.1016/j.esr.2015.03.001
- [52] Bhatt A, Priyadarshini S, Mohanakrishnan AA, Abri A, Sattler M, Techapaphawit S. Physical, chemical, and geotechnical properties of coal fly ash: A global review. *Case Studies in Construction Materials*. 2019;**11**:1-11. DOI: 10.1016/j.cscm.2019.e00263
- [53] Hall ML, Livingston WR. Fly ash quality, past, present and future, and the effect of ash on the development of novel products. *Journal of Chemical Technology and Biotechnology*. 2002;**77**: 234-239. DOI: 10.1002/jctb.538
- [54] Yao ZT, Ji XS, Sarker PK, Tang JH, Ge LQ, Xia MS, et al. A comprehensive

- review on the applications of coal fly ash. *Earth-Science Reviews*. 2015;**141**: 105-121. DOI: 10.1016/j.earscirev.2014.11.016
- [55] Thompson RL, Bank T, Montross S, Roth E, Howard B, Verba C, et al. Analysis of rare earth elements in coal fly ash using laser ablation inductively coupled plasma mass spectrometry and scanning electron microscopy. *Spectrochimica Acta Part B*. 2018;**143**: 1-11. DOI: 10.1016/j.sab.2018.02.009
- [56] Blissett RS, Rowson NA. A review of the multi-component utilization of coal fly ash. *Fuel*. 2012;**97**:1-23. DOI: 10.1016/j.fuel.2012.03.024
- [57] Vassilev SV, Vassileva CG. Methods for characterization of composition of fly ashes from coal-fired power stations: A critical overview. *Energy & Fuels*. 2005;**19**:1084-1098. DOI: 10.1021/ef049694d
- [58] Asl SMH, Javadian H, Khavarpour M, Belviso C, Taghavi M, Maghsudi M. Porous adsorbents derived from coal fly ash as cost-effective and environmentally-friendly sources of aluminosilicate for sequestration of aqueous and gaseous pollutants: A review. *Journal of Cleaner Production*. 2019;**208**:1131-1147. DOI: 10.1016/j.clepro.2018.10.186
- [59] Mondal S, Ghar A, Satpati AK, Sinharoy P, Singh DK, Sharma JN, et al. Recovery of rare earth elements from coal fly ash using TEHDGA impregnated resin. *Hydrometallurgy*. 2019;**185**:93-101. DOI: 10.1016/j.hydromet.2019.02.005
- [60] Jegadeesan G, Al-Abed SR, Pinto P. Influence of trace metal distribution on its leachability from coal fly ash. *Fuel*. 2008;**87**:1887-1893. DOI: 10.1016/j.fuel.2007.12.007
- [61] BP Energy Outlook: 2018 Edition [Internet]. 2018. Available from: <https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/energy-outlook/bp-energy-outlook-2018.pdf> [Accessed: 20 October 2019]
- [62] Ram LC, Masto RE. Fly ash for soil amelioration: A review on the influence of ash blending with inorganic and organic amendments. *Earth-Science Reviews*. 2014;**128**:52-74. DOI: 10.1016/j.earscirev.2013.10.003
- [63] Wesche K, editor. Fly Ash in Concrete: Properties and Performance. 1st ed. London: CRC Press (Taylor & Francis Group); 1991. DOI: 10.1201/9781482267051. 356p
- [64] Vichaphund S, Aht-Ong D, Sricharoenchaikul V, Atong D. Characteristic of fly ash derived-zeolite and its catalytic performance for fast pyrolysis of Jatropha waste. *Environmental Technology*. 2014;**35**: 2254-2261. DOI: 10.1080/09593330.2014.900118
- [65] Franus W, Wiatros-Motyka MM, Wdowin M. Coal fly ash as a resource for rare earth elements. *Environmental Science and Pollution Research*. 2015;**22**: 9464-9474. DOI: 10.1007/s11356-015-4111-9
- [66] Cokca E, Yilmaz Z. Use of rubber and bentonite added fly ash as a liner material. *Waste Management*. 2004;**24**:153-164. DOI: 10.1016/j.wasman.2003.10.004
- [67] Moreno N, Querol X, Andrés JM, Stanton K, Towler M, Nugteren H, et al. Physico-chemical characteristics of European pulverized coal combustion fly ashes. *Fuel*. 2005;**84**:1351-1363. DOI: 10.1016/j.fuel.2004.06.038
- [68] Chindapasirt P, De Silva P, Sagoe-Crentsil K, Hanjitsuwan S. Effect of SiO₂ and Al₂O₃ on the setting and hardening of high calcium fly ash-based geopolymer systems. *Journal of Materials Science*. 2012;**47**:4876-4883. DOI: 10.1007/s10853-012-6353-y

- [69] Terzić A, Radojević Z, Miličić LJ, Pavlović LJ, Aćimović Z. Leaching of the potentially toxic pollutants from composites based on waste raw material. *Chemical Industry and Chemical Engineering Quarterly*. 2012;**18**:373-383. DOI: 10.2298/CICEQ111128013T
- [70] Lee SH, Kim HJ, Sakai E, Daimon M. Effect of particle size distribution of fly-ash-cement system on the fluidity of cement pastes. *Cement and Concrete Research*. 2003;**33**: 763-768. DOI: 10.1016/S0008-8846(02) 01054-2
- [71] Koukoulzas NK, Zeng R, Perdikatsis V, Xu W, Kakaras EK. Mineralogy and geochemistry of Greek and Chinese coal fly ash. *Fuel*. 2006;**85**: 2301-2309. DOI: 10.1016/j.fuel. 2006.02.019
- [72] Takada T, Hashimoto I, Tsutsumi K, Shibata Y, Yamamuro S, Kamada T, et al. Utilization of coal ash from fluidized-bed combustion boilers as road base material. *Resources, Conservation and Recycling*. 1995;**14**: 69-77. DOI: 10.1016/S0921-3449(95) 80001-8
- [73] Lanyerstorfer C. Pre-processing of coal combustion fly ash by classification for enrichment or rare earth elements. *Energy Reports*. 2018;**4**:660-663. DOI: 10.1016/j.egry.2018.10.010
- [74] Hower JC, Dai S, Seredin VV, Zhao L, Kostova IJ, Silva LFO, et al. Note on the occurrence of yttrium and rare earth elements in coal combustion products. *Coal Combustion and Gasification Products*. 2013;**5**:39-47. DOI: 10.4177/CCGD-D-13-00001-1
- [75] Birik D, White JC. Rare earth elements, in bituminous coals and underclays of the Sydney Basin, Nova Scotia: Element sites, distribution, mineralogy. *International Journal of Coal Geology*. 1991;**19**:219-251. DOI: 10.1016/0166-5162(91)90022-B
- [76] Pan J, Zhou C, Tang M, Cao S, Liu C, Zhang N, et al. Study on the modes of occurrence of rare earth elements in coal fly ash by statistics and a sequential chemical extraction procedure. *Fuel*. 2019;**237**:555-565. DOI: 10.1016/j.fuel.2018.09.139
- [77] Fiket Z, Medunić G, Turk MF, Kniewald G. Rare earth elements in superhigh-organic sulfur Rusa coal ash (Croatia). *International Journal of Coal Geology*. 2018;**194**:1-10. DOI: 10.1016/j. coal.2018.05.002
- [78] Georgakopoulos A, Filippidis A, Fournaraki AK, Turiel JLF, Llorenes JF, Mousty F. Leachability of major and trace elements of fly ash from Ptolemais Power Station, Northern Greece. *Energy Sources*. 2002;**24**:103-113. DOI: 10.1080/00908310252774426
- [79] Kashiwakura S, Kumagai Y, Kubo H, Wagatsuma K. Dissolution of rare earth elements from coal fly ash particles in a dilute H₂SO₄ solvent. *Open Journal of Physical Chemistry*. 2013;**3**: 69-75. DOI: 10.4236/ojpc.2013.32009
- [80] Tuan LQ, Thenepalli T, Chilakala R, Vu HHT, Ahn JW, Kim J. Leaching characteristics of low concentration rare earth elements in Korean (Samcheok) CFBC bottom ash samples. *Sustainability*. 2019;**11**:1-11. DOI: 10.3390/su11092562
- [81] Seredin VV. Rare earth element-bearing coals from the Russian Far East deposits. *International Journal of Coal Geology*. 1996;**30**:101-129. DOI: 10.1016/0166-5162(95)00039-9
- [82] Wagner NJ, Matiane A. Rare earth elements in select Main Karoo Basin (South Africa) coal and coal ash samples. *International Journal of Coal Geology*. 2018;**196**:82-92. DOI: 10.1016/j.coal.2018.06.020
- [83] Folgueras MB, Alonso M, Fernandez FJ. Coal and sewage sludge

ashes as sources of rare earth elements. *Fuel*. 2018;**192**:128-139. DOI: 10.1016/j.fuel.2016.12.019

[84] Huang Z, Fan M, Tian H. Rare earth elements of fly ash from Wyoming's Powder River Basin Coal. *Journal of Rare Earths*. 2019;**38**:1-8. DOI: 10.1016/j.jre.2019.05.004

[85] Flues M, Sato IM, Scapin MA, Cotrim MEB, Camargo IMC. Toxic element mobility in coal and ashes of Figueira Coal Power Plant, Brazil. *Fuel*. 2013;**103**:430-436. DOI: 10.1016/j.fuel.2012.09.045

[86] Silva LFO, DaBoit K, Sampaio CH, Jasper A, Andrade ML, Kostova IJ, et al. The occurrence of hazardous volatile elements and nanoparticles in Bulgarian coal fly ashes and the effect on human health exposure. *Science of the Total Environment*. 2012;**416**:513-526. DOI: 10.1016/j.scitotenv.2011.11.012

[87] Goodarzi F. Characteristics and composition of fly ash from Canadian coal/fired power plants. *Fuel*. 2006;**85**:1418-1427. DOI: 10.1016/j.fuel.2005.11.022

[88] Tang Q, Liu G, Zhou C, Zhang H, Sun R. Distribution of environmentally sensitive elements in residential soils near a coal/fired power plant: Potential risks to ecology and children's health. *Chemosphere*. 2013;**93**:2473-2479. DOI: 10.1016/j.chemosphere.2013.09.015

[89] Medunić G, Kuharić Z, Krivohvalek A, Fiket Z, Radjenović A, Gödel K, et al. Geochemistry of Croatian superhigh-organic-sulphur Rasa coal, imported low-S coal, and bottom ash: Their Se and trace metal fingerprints in seawater, clover, foliage, and mushroom specimens. *International Journal of Oil Gas and Coal Technology*. 2018;**18**:3-24. DOI: 10.1504/IJOGCT.2018.10006334

[90] Kurda R, Silvestre JD, Brito J. Toxicity and environmental and

economic performance of fly ash and recycled concrete aggregates use in concrete: A review. *Heliyon*. 2018;**4**:1-45. DOI: 10.1016/j.heliyon.2018.e00611

[91] Petrotou A, Skordas K, Papastergios G, Filippidis A. Factors affecting the distribution of potentially toxic elements in surface soils around and industrialized area of northwestern Greece. *Environment and Earth Science*. 2012;**65**:823-833. DOI: 10.1007/s12665-011-1127-4

[92] Sushil S, Batra VS. Analysis of fly ash heavy metal content and disposal in three thermal power plants in India. *Fuel*. 2006;**85**:2676-2679. DOI: 10.1016/j.fuel.2006.04.031

[93] Kim Y, Kim K, Jeong GY. Study of detailed geochemistry of hazardous elements in weathered coal ashes. *Fuel*. 2017;**193**:343-350. DOI: 10.1016/j.fuel.2016.12.080

[94] Čujić M, Dragović S, Djordjević M, Dragović R, Gajić B. Environmental assessment of heavy metals around the largest coal fired power plant in Serbia. *Catena*. 2016;**139**:44-52. DOI: 10.1016/j.catena.2015.12.001

[95] Keegan TJ, Farago ME, Thornton I, Hong B, Colville RN, Pesch B, et al. Dispersion of As and selected heavy metals around a coal-burning power station in central Slovakia. *Science of the Total Environment*. 2006;**358**:61-71. DOI: 10.1016/j.scitotenv.2005.03.020

[96] Ayanda OS, Fatoki OS, Adekola FA, Ximba BJ. Characterization of fly ash generated from Matla Power Station in Mpumalanga, South Africa. *Journal of Chemistry*. 2012;**9**:1788-1795

[97] Penilla RP, Bustos AG, Elizalde SG. Immobilization of Cs, Cd, Pb and Cr by synthetic zeolites from Spanish low-calcium coal fly ash. *Fuel*. 2006;**85**:823-832. DOI: 10.1016/j.fuel.2005.08.022

- [98] Baba A, Kaya A. Leaching characteristics of solid waste from thermal power plants of western Turkey and comparison of toxicity methodologies. *Journal of Environmental Management*. 2004;**73**: 199-207. DOI: 10.1016/j.jenvman.2004.06.005
- [99] Hower JC, Robertson JD. Chemistry and petrology of fly ash derived from the co-combustion of western United States coal and tire-derived fuel. *Fuel Processing Technology*. 2004;**85**:359-377. DOI: 10.1016/j.fuproc.2003.05.03
- [100] Manz OE. Coal fly ash: A retrospective and future look. *Fuel*. 1999;**78**:133-136. DOI: 10.1016/S0016-2361(98)00148-3
- [101] Vassilev SV, Vassileva CG. A new approach for the combined chemical and mineral classification of the inorganic matter in coal. 1. Chemical and mineral classification systems. *Fuel*. 2009;**88**:235-245. DOI: 10.1016/j.fuel.2008.09.006
- [102] Gollakota ARK, Volli V, Shu C-M. Progressive utilization prospects of coal fly ash: A review. *Science of the Total Environment*. 2019;**672**:951-989. DOI: 10.1016/j.scitotenv.2019.03.337
- [103] Gajić G, Djudjević L, Kostić O, Jarić S, Mitrović M, Pavlović P. Ecological potential of plants for phytoremediation and ecorestoration of fly ash deposits and mine wastes. *Frontiers in Environmental Science*. 2018;**6**:1-24. DOI: 10.3389/fenvs.2018.00124
- [104] Tiwari MK, Bajpai S, Dewangan UK, Tamrakar RK. Suitability of leaching test methods for fly ash and slag: A review. *Journal of Radiation Research and Applied Science*. 2015;**8**: 523-537. DOI: 10.1016/j.jrras.2015.06.003
- [105] Ahmaruzzaman M. A review on the utilization of fly ash. *Progress in Energy and Combustion Science*. 2010;**36**: 327-363. DOI: 10.1016/j.jpeccs.2009.11.003
- [106] Abdalqader AF, Jin F, Al-Tabbaa A. Development of greener alkali-activated cement: Utilization of sodium carbonate for activating slag and fly ash mixtures. *Journal of Cleaner Production*. 2016;**113**:66-75. DOI: 10.1016/j.clepro.2015.12.010
- [107] Huang X, Zhao H, Zhang G, Li J, Yang Y, Ji P. Potential of removing Cd (II) and Pb(II) from contaminated water using a newly modified fly ash. *Chemosphere*. 2020;**242**:125148. DOI: 10.1016/j.chemosphere.2019.125148
- [108] Cardoso AM, Paprocki A, Ferret LS, Azevedo CMN, Pires M. Synthesis of zeolite Na-P1 under mild conditions using Brazilian coal fly ash and its applications in wastewater treatment. *Fuel*. 2015;**139**:59-67. DOI: 10.1016/j.fuel.2014.08.016
- [109] Mushtaq F, Zahid M, Bhatti IA, Nasir S, Hussain T. Possible applications of coal fly ash in wastewater treatment. *Journal of Environmental Management*. 2019;**240**:27-46. DOI: 10.1016/j.envman.2019.03.054
- [110] Belviso C. State-of-the-art applications of fly ash from coal and biomass: A focus on zeolite synthesis processes and issues. *Progress in Energy and Combustion Science*. 2018;**65**: 109-135. DOI: 10.1016/j.peccs.2017.10.004
- [111] Tauanov Z, Shah D, Inglezakis V, Jamwal PK. Hydrothermal synthesis of zeolite production from coal fly ash: A heuristic approach and its optimization for system identification of conversion. *Journal of Cleaner Production*. 2018;**182**: 616-623. DOI: 10.1016/j.clepro.2018.02.047
- [112] Iqbal A, Sattar H, Haider R, Munir S. Synthesis and characterization of pure phase zeolite 4A from coal fly

- ash. *Journal of Cleaner Production*. 2019;**219**:258-267. DOI: 10.1016/j.clepro.2019.02.066
- [113] Feng W, Wan Z, Daniels J, Li Z, Xiao G, Yu J, et al. Synthesis of high quality zeolites from coal fly ash: Mobility of hazardous elements and environmental applications. *Journal of Cleaner Production*. 2018;**202**:390-400. DOI: 10.1016/j.clepro.2018.08.140
- [114] Fukasawa T, Horigome A, Tsu T, Karisma AD, Maeda N, Huang A-N, et al. Utilization of incineration fly ash from biomass power plants for zeolite synthesis from coal fly ash by hydrothermal treatment. *Fuel Processing Technology*. 2017;**167**:92-98. DOI: 10.1016/j.fuproc.2017.06.023
- [115] Ojumu TV, Du Plessis PW, Petrik LF. Synthesis of zeolite A from coal fly ash using ultrasonic treatment—A replacement for fusion step. *Ultrasonics Sonochemistry*. 2016;**31**: 342-349. DOI: 10.1016/j.ultsonch.2016.01.016
- [116] Babajide O, Musyoka N, Petrik L, Ameer F. Novel zeolite Na-X synthesized from fly ash as a heterogeneous catalyst in biodiesel production. *Catalysis Today*. 2012;**190**: 54-60. DOI: 10.1016/j.cattod.2012.04.044
- [117] Manique MC, Lacerda LV, Alves AK, Bergmann CP. Biodiesel production using coal fly ash-derived sodalite as a heterogeneous catalyst. *Fuel*. 2017;**190**:268-273. DOI: 10.1016/j.fuel.2016.11.016
- [118] Chakraborty R, Bepari S, Banerjee A. Transesterification of soybean oil catalyzed by fly ash and egg shell derived solid catalyst. *Chemical Engineering Journal*. 2010;**165**:798-805. DOI: 10.1016/j.cej.2010.10.01
- [119] Xiang Y, Wang L, Jiao Y. Ultrasound strengthened biodiesel production from waste cooking oil using modified coal fly ash as catalyst. *Journal of Environmental Chemical Engineering*. 2016;**4**:818-824. DOI: 10.1016/j.jece.2015.12.031
- [120] Bhandari R, Volli V, Purkait MK. Preparation and characterization of fly ash based mesoporous catalyst for transesterification of soybean oil. *Journal of Environmental Chemical Engineering*. 2015;**3**:906-914. DOI: 10.1016/j.jece.2015.04.008
- [121] Volli V, Purkait MK, Shu CM. Preparation and characterization of animal bone powder impregnated fly ash catalyst for transesterification. *Science of the Total Environment*. 2019;**669**:314-321. DOI: 10.1016/j.scitotenv.2019.03.080
- [122] He PY, Zhang YJ, Chen H, Han ZC, Liu LC. Low-energy synthesis of kaliophilite catalyst from circulating fluidized bed fly ash for biodiesel production. *Fuel*. 2019;**257**:1-10. DOI: 10.1016/j.fuel.2019.116041
- [123] Babajide O, Musyoka N, Petrik L, Ameer F. Use of coal fly ash as a catalyst in the production of biodiesel. *Petroleum and Coal*. 2010;**52**:261-272
- [124] Kotwal MS, Niphadkar PS, Deshpande SS, Bokade VV, Joshi PN. Transesterification of sunflower oil catalyzed by flyash-based solid catalysts. *Fuel*. 2009;**88**:1773-1778. DOI: 10.1016/j.fuel.2009.04.004
- [125] Algoufi YT, Hameed BH. Synthesis of glycerol carbonate by transesterification of glycerol with dimethyl carbonate over K-zeolite derived from coal fly ash. *Fuel Processing Technology*. 2014;**126**:5-11. DOI: 10.1016/j.fuproc.2014.04.004
- [126] Helwani Z, Fatra W, Saputra E, Maulana R. Preparation of CaO/Fly ash as a catalyst inhibitor for transesterification process of palm oil in

biodiesel production. IOP Conference Series: Materials Science and Engineering. 2018;**334**:1-10

[127] Volli V, Purkait MK. Preparation and characterization of hydrotalcite-like materials from flyash for transesterification. Clean Technologies and Environmental Policy. 2016;**18**: 529-540. DOI: 10.1007/s10098-015-1036-4

[128] Hadiyanto H, Lestari SP, Abdullah A, Widayat W, Sutanto H. The development of fly ash-supported CaO derived from mollusk shell of *Anadara granosa* and *Pahia undulate* as heterogeneous CaO catalyst in biodiesel synthesis. International Journal of Energy and Environmental Engineering. 2016;**7**:297-305. DOI: 10.1007/s40095-016-0212-6

[129] Lathiya DR, Bhatt DV, Maheria KC. Sulfated fly-ash catalyzed biodiesel production from maize acid feedstock: A comparative study of Taguchi and Box-Behnken design. ChemistrySelect. 2019;**4**:4392-4397. DOI: 10.1002/slct.201803916

[130] Volli V, Purkait MK. Selective preparation of zeolite X and A from fly ash and its use as catalyst for biodiesel production. Journal of Hazardous Materials. 2015;**297**:101-111. DOI: 10.1016/j.hazmat.2015.04.066