

# Applications of Solid Wastes based Heterogeneous Catalyst: A review

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*Abstract*—Solid wastes arose as an apprehension nowadays because of their handling and disposal issues. The major solid wastes are eggshell, fly ash, oil palm based wastes and rice husk ash, which are discarded over million tonnes around the world. Rather than to be served as no economic value waste, these residues consist of high silica content, which prompted its other applications, such as its adoption as an economical and environmental-friendly catalyst. In the present work, an attempt to provide an overview of the applications of solid wastes as heterogeneous catalysts in various processes was done. According to the literature reviewed, the vast feasibility of the solid wastes as heterogeneous catalysts was proven, in which tremendous variation of highly valuable products could be obtained via the assistance of the synthesized cheap and green catalysts. The reported literature provided a benchmark for further widen the possible applications of these solid waste based heterogeneous catalysts.

*Keywords*— *Solid wastes; Heterogeneous catalysts, Applications*

## 1. INTRODUCTION

The limitation and the awareness towards environmental conservation and preservation in the recent decade have urged the researchers to find alternative fuel. The demand for porous materials is kept escalating in parallel with the alternative fuel exploring, thus led to immense focus towards comparative efficiencies, inexpensive materials. Generally, the major silica composition in porous materials was originated from commercially alkoxy silane compounds such as sodium silicate, tetraethylorthosilicate (TEOS) as well as tetramethylorthosilicate as reported in the literature [1]. Regrettably, these silica precursors are detrimental to human body due to its high toxicity, in which only a mild exposure can cause death [2]. Therefore, economic and environmentally friendly and even safe handling alternatives need to be identified. Major solid wastes such as eggshell, fly ash, oil palm based wastes and rice husk ash contain natural silica source, which are the keys to act as natural silica precursors' replacement. Thereupon, the abundant and cheap freely acquired silica alternatives from those solid wastes have been adopted in heterogeneous catalysts synthesis for vast applications. To the best of our knowledge, to date, there is almost no literature review on the applications of several types of solid wastes based heterogeneous catalyst. Intentionally, this review paper focuses on the discussion and comparison of the catalyst preparations and reaction performance of various solid wastes based catalysts. The successful synthesis and applications of green, inexpensive heterogeneous catalysts will be discussed to provide a benchmark for future exploration of their applications in wide-ranging fields.

## 2. EGGSHELL CATALYSTS

Eggshell is basically made up 10% of an egg, in which it was produced in bulk quantity by egg processing industries, thus resulted vast quantity of this solid waste was dumped as trash in landfills. This disposal method in the absence of any pretreatment raised the issue of organic contamination [3, 4]. Generally, the eggshell is a perfectly aligned polycrystalline structure throughout the calcined shell, which can be considered as a natural porous bioceramic [5]. The composition of eggshell composed of approximately 96% calcium carbonate, minor quantities of calcium phosphate, organic components (mainly proteins), water and magnesium carbonate [4]. The superfluous no economic value eggshell solid residues prompted an

appropriate approach to minimize the disposal issue of this material. The applications of eggshell catalysts in various reactions are summarized in Table 1.

Taufiq-Yap and co-authors [6] evaluated the performance of eggshell catalyst towards hydrogen generation through wood gasification [6]. The study was done in conjugation with the challenge of reducing problematic CO<sub>2</sub> that contributed to the major composition of greenhouse gases, which emitted via anthropogenic activities, therefore a lot of attention has been focused on the development of clean alternative fuel such as hydrogen. Particularly, hydrogen generation through gasification is a fascinating research matter in the past few ten years, in which these processes can be enhanced with the assistance of catalysts [7]. Therefore, impregnation of CaO was done on the eggshell catalyst support and then carried out *Azadirachta excelsa* wood biomass gasification. Few gases (H<sub>2</sub>, CH<sub>4</sub>, CO, and CO<sub>2</sub>) were yielded from the biomass decomposition, accompanied with some side products such as tar and coke. CO<sub>2</sub> production was suppressed for eggshell catalyzed reaction as compared to reaction without a catalyst, which was absorbed by CaO and thus stimulated water gas shift reaction to generate H<sub>2</sub>. Tar and coke gasification resulted in an increment in the gaseous product also promoted by eggshell catalysts. Maximum hydrogen yield was 73% which increased with the increment in catalyst loading.

Likewise, methane emerged as another potential reactant to produce syngas (H<sub>2</sub>+ CO), in which methane can be generated by organic wastes anaerobic digestion or obtained in natural gas preserves [8]. Therefore, in term of economic and technical aspects, partial oxidation of methane (POM) is an advantageous route for syngas production [9]. Consequently, Karoshi and co-researchers [9] inspected the catalytic performance of eggshell catalyst after calcined over POM in a packed bed reactor [9]. Higher hydrocarbons (C<sub>2</sub>-C<sub>7</sub>) were yielded by the means of the POM on calcined eggshell. Additionally, the authors indicated oxidative coupling of methane happened to convert the methane into ethylene and ethane, which was even altered to C<sub>3</sub>-C<sub>7</sub> hydrocarbons through aromatization or coupling. In the work, it was also signified that particular orientation magnitude could be preserved by the calcined eggshell's CaO active sites which procured surface bound aromatization or coupling processes.

Furthermore, dimethyl carbonate (DMC) appeared as a crucial carbonylating and methylating agent on account of its unsatisfactory bioaccumulation and persistence, biodegradability and its less toxicity. Interestingly, unfavorable phosgene in the synthesis of polycarbonate dimethylsulfate and methylhalides in methylation reactions can be replaced by DMC[3]. In the year of 2012, Gao and Xu [3] developed an eggshell-based catalyst for DMC synthesis by the methanol and propylene carbonate transesterification. Under the optimum conditions (0.8 wt% eggshell catalyst, 10:1 molar ratio of methanol/propylene carbonate, ambient temperature, and pressure), the propylene carbonate conversion and the DMC yield were 80 and 75%, respectively after 1 h.

In the meantime, different bioactive compounds can also be synthesized by eggshell based catalysts. 2-aminochromenes was produced under thermal solvent-free condition using eggshell, as reported by Mosaddegh [10]. Sonicated eggshell was found to perform better reaction than CaCO<sub>3</sub> and ball milling obtained eggshell powder. It is worth mentioning that up to six times regeneration can be performed without any activity loss. Additionally, this same author [11] synthesized 7,8-dihydro-4H-chromen-5(6H) ones at room temperature by employing eggshells as a catalyst. This catalyst could be repeatedly used for five cycles while maintained the high performance.

Meanwhile, prebiotic lactulose obtained from lactose isomerization aid in inhibiting pathogenic bacteria such as Salmonella in the body, at the same time stimulating the lactobacilli and bifidobacteria growth in the gastrointestinal tract [12, 13]. Montilla et al. [14] inspected the influence of loadings of catalyst, pH as well as lactose concentration over lactose isomerization, by adopting eggshell based catalyst. After 90 min time-on-stream (TOS) and 98 °C reaction temperature, 25% lactulose production was accomplished from milk permeate by adopting catalyst loading of 4 mg/mL. In the same year, lactulose was obtained by Nooshkam and Madadlou [15] via ultrafiltration permeate of milk using the same protocols [15]. Roughly 17% conversion of lactose were transformed lactulose. Thereafter, lactose crystallization by methanol was done to purify the isomerized permeate to a lactulose-rich product. Hence, the study indicated the potential of eggshell as a catalyst for lactulose production via lactose isomerization.

Intriguingly, eggshells solid waste can also be used for waste (soil, water, and air) treatment and environmental protection by playing the role as an adsorbent. Eggshell adsorbent can effectively remove a wide range of pollutants such as heavy metals, dyes, pesticides, phenols, organic and inorganic compounds. For instance, calcium zeolite type A (CaNaAlSi<sub>2</sub>O<sub>7</sub>) was synthesized by the sol-gel method by employing the starting material of CaO yielded via the pyrolysis of chicken eggshells [16]. The synthesized eggshell adsorbent was physically and chemically comparable with commercial zeolites, with the specific surface area and the average pore diameter were 55.15 m<sup>2</sup>/g and 37.19 nm, respectively. These authors confirmed the feasibility of eggshell based catalyst in wastewater treatment.

**Table 1:** Comparison of eggshell catalyst found in the literature.

Product	Catalyst preparation	Process	Reference
Hydrogen	Wash with deionized water, eliminate the membrane, ground and sieve (250 mm), dry and calcine (900 °C, 2 h).	Wood gasification	[6]
Syngas	Rinse using deionized water, dry and calcine (100 °C, 4 h)	Partial oxidation of methane	[9]
Dimethyl carbonate	Rinse using deionized water, dry (100 °C, 24 h), calcine (1000 °C, 2 h) and ground.	Propylene carbonate and methanol transesterification	[3]
2-aminochromenes	Wash with deionized water, eliminate the membrane, dry (120 °C, 1 h). Crush and mix the CH <sub>2</sub> Cl <sub>2</sub> with eggshell powder, put in an ultrasonic bath (50 °C, 60 Hz, 1 h), filter and dry at ambient temperature.	Heterogeneous base catalyzed organic synthesis	[10]
7,8-dihydro-4H-chromen-5(6H)-ones	Wash with deionized water, eliminate the membrane, dry at ambient temperature. Ground and crush by pestle mortar.	Heterogeneous base catalyzed organic synthesis	[11]
Lactulose	Wash with deionized water, dry (105 °C, 4-24 h), crush and sieve (~5 mm)	Lactose isomerization	[14]
	Wash with deionized water, dry (105 °C, 12 h), crush and sieve (177 mm)		[15]
-	Eggshell as the starting material, catalyst was synthesized with CaO: Al <sub>2</sub> O <sub>3</sub> : Na <sub>2</sub> O: SiO <sub>2</sub> of 1:1:2:8 molar ratio using the sol-gel method. Calcine at (300 °C, 1 h).	Reduction of dyes in wastewater	[16]

### 3. COAL FLY ASH CATALYSTS

Coal fly ash (CFA), which also known as bottom ash are waste residue generated from electric power, coal and biomass combustion [17]. The various metal oxides composition in CFA possesses high thermal stability, with a major composition made up of aluminosilicates [18]. Therefore, CFA has exceptional potential to be employed as praiseworthy porous catalysts by impregnation with other active components and adsorbents, owing to its high aluminum and silicon content. In each year, bulky quantities of CFA are generated and disposed of in the land and subsequently lead to long-term financial burden and environmental impacts. Therein, a great interest has been devoted to the vast utilization of CFA in catalytic reaction as listed in Table 2.

The catalytic performance of CFA was studied by Chen et al. [19] as early 1980 over the steam reforming of methane and water-gas shift reaction using a fluidized bed reactor at the temperature range of 370-900 °C. In fact, steam reforming of methane and water-gas shift reaction are one of the principal gas phase reactions in syngas production. Iron-based catalysts are proven with its efficiency for these reactions [20]. CFA catalysts successfully catalyzed both reactions, in which the reactions rates for both reactions were few times fold of the corresponding non-catalytic reactions. Moreover, CFA catalyst led to the water-gas shift reaction was dominant over steam reforming of methane reaction, owing to the larger quantity of iron oxide in the CFA.

Meanwhile, Kastner et al. [21] applied CFA as a heterogeneous catalyst for catalytic oxidation of odorous sulfur compounds [21]. The result indicated that CFA successfully catalyzed the H<sub>2</sub>S and ethanethiol oxidation at room temperature (23-25 °C). In a continuous packed bed reactor, inlet 400-500 ppmv H<sub>2</sub>S concentration of a gaseous stream was diminished to 200 ppmv within 4.6 s residence time. 50% removal efficiency remained within 4.6 time-on-stream (TOS). Similarly, Kolar et al. [22] also employed wood fly ash as a catalyst for catalytic air oxidation in and aldehydes catalytic ozonation [22]. 2-methylbutanal (2-MB) and 3-methylbutanal (3-MB) as typical volatile organic compounds (VOCs) were tested using wood fly ash in catalytic air oxidation. First order overall oxidation rate appeared with respect to 3-MB for 3-MB continuous catalytic oxidation using wood fly ash. Furthermore, 20% representative conversion of 67 ppmv inlet concentration and 2 s residence time at 25°C, 1 atm, GHSV 1800 h<sup>-1</sup> was achieved [22].

On the other hand, Babajide et al. [23] presented the utilization of CFA dumped in South Africa to produce biodiesel (methyl esters) via sunflower oil transesterification reaction with methanol [23]. A maximum oil conversion of 86.13% at a reaction temperature of 160°C for 5% wt KNO<sub>3</sub> loaded CFA based catalyst. The fuel natures of the methyl esters (biodiesel) synthesized

were tested and compared with ASTM biodiesel standard. The overall biodiesel production cost was reduced greatly due to the easy separation of catalysts and combined application in continuous process.

It is a publicity-known that wet oxidation (WO) with H<sub>2</sub>O<sub>2</sub> and air process is vital for the chlorophenol and other organic contaminants mineralization in water. Deka et al. [24] synthesized catalysts by using solid waste by a thermal power plant, CFA as the support and then impregnated with three divalent metal cations, Ni(II), Co(II) and Mn(II), and separately for 4-chlorophenol (4-CP) mineralization [24]. The catalytic performance of the catalysts were examined under several parameters such as catalyst loading, feed concentration, reaction time, temperature, pH and 4-CP/H<sub>2</sub>O<sub>2</sub> reactant mole ratio. The activity of the catalysts declined with the trend of Ni(II)-fly ash > Co(II)-fly ash > Mn(II)-fly ash. Almost 50 % 4-chlorophenol (4-CP) oxidative destruction was achieved at 5×10<sup>-3</sup> M concentration (which is equivalent to ~640 mg L<sup>-1</sup>) with equimolar hydrogen peroxide by a CFA-based catalyst, even under different reaction conditions. As soon as the hydrogen peroxide to 4-CP mole proportion increased to 20, the oxidation ameliorated to more than 90%.

In the meantime, the biodiesel production is usually executed by refined vegetable oils transesterification with methanol with the aid of homogeneous or heterogeneous base catalysts. Helwani et al. [25] make use of the abundant quantity of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in CFA to be employed as low-cost catalyst support [25]. Impregnation of CaO of calcium nitrate tetrahydrate (Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O) onto the CFA successfully synthesized an efficient catalyst. The effect of calcination temperature and Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O and CFA weight ratio determined the optimum catalyst preparation conditions. Results indicated highest activity of the catalyst was marked at 800 °C calcination temperature and 80:20 of Ca(NO<sub>3</sub>)<sub>2</sub>.4H<sub>2</sub>O to fly ash proportion. 71.77% biodiesel yield attained under 6 wt% catalyst dosage, a reaction temperature of 70 °C for 2 h and oil: methanol ratio of 1:6.

**Table 2:** Comparison of fly ash catalyst found in the literature.

Product	Catalyst Preparation	Process	Reference
Syngas	Pulverize, sieve (~40 and 100 mesh), calcine (1000 °C, 2 h)	Steam reforming of methane and water-gas shift reaction.	[19]
	Rinse with deionized water, dry (100 °C, 24 h), calcine (1000 °C, 2 h) and ground.	Catalytic Oxidation of Hydrogen Sulfide and Methanethiol	[21]
-	Lignite as feedstock, no any pretreatments on the materials.	Catalytic oxidation of aldehydes	[22]
Biodiesel	Wet impregnation with different loadings % of potassium on fly ash.	Sunflower oil transesterification	[23]
-	Wash, reflux with solution of Mn(II), Co(II) and Ni(II) separately (40 ml, 1.0 M, 6 h). Filter, wash and dry.	4-chlorophenol mineralization	[24]
Biodiesel	Impregnation method with different loadings % of calcium nitrate tetrahydrate (Ca(NO <sub>3</sub> ) <sub>2</sub> .4H <sub>2</sub> O) on fly ash.	Transesterification process off palm oil	[25]

#### 4. OIL PALM BASED CATALYSTS

Palm oil industry is one of the major agro-industry in Southeast Asia in which this industry generated a tremendous quantity of wastes such as empty fruit bunches (EFB), oil palm fibers, and oil palm shells [26]. In the meantime, palm oil fuel ash (POFA) was acquired when palm oil kernel shell and palm oil husk were subjected to burning in palm oil mill boilers. However, this conventional method to dispose of oil palm wastes raised severe environmental issues, owing to excessive black soot and large amounts of ash produced during combustion [27]. Therefore, researchers proposed numerous oil palm wastes utilization to alleviate the negative impacts from the disposal problem. Summaries of the utilization of oil palm waste as a solid catalyst in the catalytic reaction were tabulated in Table 3.

As shown in Table 3, the vast feasibility of palm-oil based catalysts involved the utilization oil palm kernel shell (OPKS) as catalyst support for FAME production by Kathirvel et al. [28] at distinct oil to catalyst loadings and reaction temperatures [28]. Generally, biodiesel is a form of diesel fuel, which mainly consists of fatty acid methyl ester (FAME) produced by catalyzed vegetable oil transesterification reaction with methanol. FAME attracted considerable attention among researchers and industries, as it is non-toxic, low emissions, carbon-neutral renewable and biodegradable [29]. Percentage of FAME produced indicated the successful NaOH incorporation of on OPKS. The experiment was conducted in a batch system which involved the parameters of ratio catalyst to oil (1-3 wt %), reaction temperature (30-60 °C), molar ratio oil to methanol (1:6-1:12) and reaction time (3-6 h). The potential of oil palm based catalyst to be used as an active catalyst to yield FAME was proven.

In addition, Ho et al. [30] investigated on the performance of palm oil mill ash (POFA) supported on CaO on biodiesel production through the transesterification of crude palm oil (CPO) [30]. The optimum catalyst preparation conditions were

found to be at 850 °C calcination temperature for 2 h with 45 wt.% calcined calcium carbonate (CaCO<sub>3</sub>). 79.76% biodiesel yield and 97.09% FAME conversion were marked at the transesterification conditions of 6 wt.% catalyst loading, 3 h reaction time, 45 °C reaction temperature, 12:1 methanol to oil molar ratio and 700 rpm stirring speed. Regenerated catalyst by washing with methanol followed by re-calcination at 850 C for 2 h was reused up to three subsequent cycles without significant reaction loss. This study further evidenced low-cost heterogeneous POFA based catalyst has vast feasibility for transesterification purposes.

On the other hand, Maniam et al. [31] conducted a research on the methyl esters production using oil palm fruit ash (OPFA), OPFA supported by rice husk silica (OPFA-RHS) and potassium-OPFA-RHS as catalysts through transesterification process using waste frying oil [31]. In comparison with homogeneous alkali catalysts, the catalysts adopted higher stability activity. 3 % catalyst loadings of OPFA and K-OPFA-RHS; 5 % catalyst loading of OPFA-RHS; 9:1 methanol to oil molar ratio; and 2h reaction time were found to be the optimum conditions for the reaction. 96.6–98.2 % process conversion was achieved at 65 °C to transesterify oil to methyl esters. High reusability up to 5 cycles shown by the catalysts with up to 83% of methyl esters. Regeneration of the catalysts was performed in an easy way by simple filtration to separate out the catalysts from the reaction mixtures.

Previously, heavy metal ions contaminated wastewater was treated using an effective adsorbent, activated carbon. In recent years, this effective but costly activated carbon was replaced by low-cost adsorbent materials such as fly ash derived from the coal and agricultural wastes combustion. The capacity of these materials to remove heavy metal ions from aqueous solutions have been examined [32, 33]. The attempt to remove the organic or inorganic contaminants by using adsorbents derived from high abundance solid wastes as low-cost adsorbents is the most encouraging idea. Chu et al. [34] examined the performance of POFA as adsorbent over Cr (III) and Zn (II) heavy metals removal [34]. Results indicated that maximum adsorption capacities of ash for Cr(III) and Zn(II) removal were 251.6 and 126.7 u.mol/g dry weight ash respectively. Zn(II) uptake was significantly suppressed in the presence of Cr(III) as indicated in binary metal adsorption studies. In addition, Salleh et al. (2018) also utilized POFA as high efficient adsorbent over Hg (II) ions removal from wastewater [35]. 98.93% of mercury removal has successfully achieved under the optimum condition at 5 hr contact time and 150 rpm agitation, declared the excellent Hg (II) ions adsorption capability of POFA. The potential of POFA for mercury removal in wastewater has been proven.

Previous literature has also reported on the critical effects of 4-nitrophenol, which is an effluent generated from petrochemicals, pharmaceuticals, petroleum refineries, coke oven, steel foundry, pesticides, preservatives and other industries [36]. Al-Aoh et al. [37] studied the 4-nitrophenol removal from an aqueous solution using activated POFA as economical adsorbent [37]. The dynamical adsorption behavior of 4-nitrophenol followed the pseudo-second-order kinetic model corresponding to the correlation coefficients values. Activated POFA was verified as a promising low-cost adsorbent for wide range 4-nitrophenol concentrations removal from aqueous solutions.

**Table 3:** Comparison of palm oil-based catalyst found in the literature.

Product	Catalyst preparation	Process	Reference
Fatty acid methyl ester	Wash, dry OPKS (120 °C, 3 h), carbonize at furnace (600°C, 3 h). Grind and sieve (~1-2 mm).	Transesterification process of palm oil with methanol	[28]
	Sieve and dry POFA (105 °C, 24 h). Wet impregnation method of 45 wt.% calcined CaCO <sub>3</sub> .	Transesterification of crude palm oil	[30]
Methyl esters	Wash and dry OPF (105 °C), calcine (500, 600 and 700 °C, for 5 h).	Transesterification of Waste Frying Oil.	[31]
-	Rinse POFA with water, sieve (~ 0.5-1.0 mm).	Heavy metals removal from wastewater	[34]
-	Wash, dry POFA (110 °C for 24 h), activate by H <sub>2</sub> SO <sub>4</sub> (0.5 M, 24 h).	Mercury removal from wastewater	[35]
-	Sieve POFA (~200 and 150 µm), wash and dry (118°C, overnight), activated by the amino silane coupling agent	4-nitrophenol adsorption	[37]

## 5. RICE HUSK ASH CATALYSTS

Rice husk (RH) is the outer sheaths that form on rice grains amid their growth while was eliminated during the processing process. In general, RH made up by 20% of ash, 38% of cellulose, 22 % lignin and other organic components [38, 39]. Rice husk ash (RHA) was obtained through the burning of the rice husk, in which much of the RHA produced being dumped as waste. Lately, approximately 70 millions tonnes of RHA was yielded each year [40], in parallel with around 220 kg (22%) of husk yielded per 1000 kg of paddy milled [41]. Regrettably, the abundant RHA has resulted in severe environmental pollution and disposal issue due to the open burning and landfill of RHA. RHA with no economic value has recently gained significant attraction in terms of low cost, eco-friendly catalysts/supports for various applications [38, 42].

Table 4 tabulates the various researches have been done on the RHA catalysts. Chen et al. [43] have reported on the utilization of RHA as support for synthesis of a solid base catalyst to aid the catalytic conversion of palm oil into biodiesel [43]. Publicity known, biodiesel emerged as a promising renewable and clean biofuels, which can be obtained through refined vegetable oils transesterification with methanol with the addition of homogeneous/heterogeneous base catalysts [44]. In the research, several parameters such as the catalyst preparation method, calcination temperature, reaction conditions and catalyst reusability were studied. Results indicated that around 91.5% of biodiesel was yielded under the reaction conditions of 4 h time-on-stream (TOS), 7 wt.%, catalyst loading and methanol-to-oil molar ratio of 9:1. Even though the catalyst was being reused for up to 8 cycles, the excellent performance of biodiesel yield was achieved with above 80%. On the other hand, bio-oil was obtained through the catalytic pyrolysis studies executed on Brunei RHA in a fixed-bed pyrolysis rig as reported by Abu Bakar and Titiloye [45]. In fact, the highly oxygenated, corrosive, comparatively unstable free-flowing bio-oils consist of organic components such as aromatic hydrocarbons, esters, alcohols, ketones, organic acids, furans and anhydro-sugars [46-48]. There are improvements in term of the acidity, viscosity as well as heating values of the bio-oil as evidenced in the catalytic pyrolysis studies conducted on rice husks. This can be claimed to the RHA's high ash content, it can be served as a cheaper alternative to the zeolite catalysts to enhance the quality of bio-oil.

On the other hand, hydrogenation is one of the strategies for chemical conversions of CO<sub>2</sub>, which also considered as the crucial step in offering sustainable energy and environmental development. In fact, fuels and valuable chemicals have resulted via the reaction by the increment quantity of CO<sub>2</sub> in the atmosphere [46]. Chang et al. [49] investigated the application of RHA supported Nickel catalyst using deposition-precipitation technique over CO<sub>2</sub> hydrogenation with the H<sub>2</sub>/CO<sub>2</sub> (4/1) mixture [49]. 80% high selectivity for CH<sub>4</sub> formation was demonstrated for the reaction at the reaction temperatures ranged 673-873 K. The influence of the reduction and calcination temperatures, nickel loading quantity and deposition-precipitation time were also studied exhaustively. From the temperature-programmed desorption techniques and reaction performance, RHA has proven to be a promising alternative over silica gel as a catalysts support. In addition, Maheswari and co-researchers [50] also reported the usage of an eco-friendly, reusable, biodegradable and efficient heterogeneous catalyst, bamboo RHA on the tetrahydro-4H-chromene-3-carbonitriles synthesis. The reaction involved was the one-pot three-component reaction of malononitrile with aromatic aldehydes and dimedone or 1,3-cyclohexanedione. In the past decades, strong interest has been paid on the synthesis of tetrahydro-4H-chromene-3-carbonitrile derivatives owing to their vast of biological and pharmacological properties range, such as anticancer, anticoagulant, spasmolytic, and antianaphylactin activity. The only slight decline in catalytic activity was noticed when bamboo RHA was reused for seven times.

Moreover, the high bioaccumulation of toxic and highly distributed environmental contaminants, chlorinated organic pollutants affected the ozone layer in the atmosphere. This issue also raised the humanity concern towards environmental and health. As such, their widespread usage is a major cause of environmental and health concern. Thus, it is utmost important to important to detoxify such species using eco-friendly approach. Thabet et al. [51] proposed the chlorobenzene detoxification in a glass capillary reactor using RHA supported platinum (RHA-Pt) and titanium (RHA-Ti) as catalysts. Optimization of various detoxification experimental conditions was done as well. In comparison with 24 h reaction time marked by conventional catalysis, only 20 min was needed to completely detoxify chlorobenzene in the capillary microreactor using RHA supported catalysts [51].

In the meantime, the fast-growing rice mills industries which built the world-class economy was always accompanied by a large amount of pollutant-filled toxic wastewater being generated. Rice mills are the fast-growing industries that play a key role in shaping the progress of world economy [52]. In order to address this challenge, the Fenton-like process was performed using the RHA-supported iron catalyst as an eco-benign and economically efficient approach for the rice mill wastewater treatment. Satisfactory results were achieved with the 75.5 % of maximum COD reduction under response surface-optimized conditions of 4.12 g/L catalyst dose, 4.2 g/L H<sub>2</sub>O<sub>2</sub> concentration and pH 3.2. The study has successfully proposed an applicable scheme towards various waste generated from rapidly growing rice mills [52].

Meanwhile, ionic liquid immobilization at the solid surface is an advantageous technique to combine the beneficial natures of ionic liquids and solid properties [53]. Shirini et al. [53] used RHA as natural silica support for the 1-methyl-3-(trimethoxysilylpropyl)-imidazolium hydrogen sulfate immobilization. In very short reaction times, the products were produced in high yield and none of catalysis activity loss even though reused for ten times. The experiments further convinced the high thermal stability and regeneration of RHA-[pmim]HSO<sub>4</sub> catalyst to be applied in other organic reactions. Interestingly, partial oxidation of methanol (POM) was carried out by deposition-precipitation method synthesized ZnO-promoted copper catalysts supported on rice husk ash (Cu/ZnO/RHA) to yield hydrogen by Chen et al. [54]. Optimization of the ZnO promoter amount, pH, calcination and reaction temperatures over the catalytic activity of the Cu/ZnO/RHA catalysts was accomplished. Cu/ZnO/RHA catalysts showed comparable activity and selectivity with that of Cu/ZnO/SiO<sub>2</sub> catalysts. This was related to the high copper surface area and copper dispersion on the RHA support surface with led to the stabilization of ZnO on support.

**Table 4:** Comparison of rice husk ash catalyst found in the literature.

Product	Catalyst preparation	Process	Reference
Biodiesel	Filter, air-dried (105 °C until constant weight), calcine (400 °C, 600 °C and 800 °C) for 4 h.	Transesterification of palm oil	[43]
Bio-oil	Calcine (550 °C, 3 h), ground and mix with montmorillonite clay binder (ratio of 3:1).	Catalytic pyrolysis	[45]
Fuel	Extracted silica by acid leaching, pyrolysis, and carbon-removing processes.	Hydrogenation of CO <sub>2</sub>	[49]
Tetrahydro-4H-chromene-3-carbonitriles	Filter, air-dried (105 °C, 12 h), calcine (800 °C, 4 h).	Component reaction of malonitrile with aldehydes and 1,3-cyclohexanedione	[50]
-	Extract silica by modified advanced alkali extraction process.	Chlorobenzene detoxification	[51]
-	Extract silica by modified advanced alkali extraction process.	Fenton-like process	[55]
Formamides	Suspend in dry CH <sub>2</sub> Cl <sub>2</sub> (20 mL). Add concentrated H <sub>2</sub> SO <sub>4</sub> (97%, 2.9 mmol) in an ice bath.	N-formylation of amines	[53]
Hydrogen	Using deposition-precipitation method.	Partial oxidation of methanol	[54]

## 6. CONCLUSION

In this work, the utilization of four solid wastes – eggshell, rice husk ash, oil palm waste and coal fly ash as heterogeneous catalysts were presented. The broad pathway was found for utilization of these highly abundant solid wastes, owing to its high silica content and inappropriate disposal in landfill or open-burning. The vast amount of published experimental data verified the strong capabilities of those solid wastes in catalyzing chemical conversion reactions, synthesizing fine chemical components and environmental pollutants. It can be predicted that the solid wastes will be generated in increasing amount and will deteriorate the environmental concerns, increase disposal costs and even insufficient landfill space. Thus, new technologies have been developed to recycle and convert the solid waste into value-added products, such as an efficient catalyst to minimize the dependence on the non-renewable sources. To conclude, the successful applications of the solid wastes provided a new prospect for their future applications in various fields.

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