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Zeolite for Agriculture Intensification and Catalyst in Agroindustry

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ABSTRACT

The role of renewable products is becoming important because the fossil resources in which most of our chemicals derived is vanishing. Agriculture as the renewable sources is needed to increase the production which is not only required to meet the food demands but also to replace chemicals derived from fossil sources. Zeolite has a huge potential for agriculture intensification and conversion of agriculture products and by-products into chemicals. Indonesia has two kind deposit of natural zeolites, which are clinoptilolite and mordenite lies aligned volcanic mountain across Sumatra, Java, Nusa Tenggara, and Sulawesi Islands. Zeolite has a large surface area consisted of microporous and mesoporous structures. It could be utilized as an ion exchange agent, adsorbent and catalyst for applications in agriculture and agroindustry. Sustainable development of agricultural products could be also assisted by zeolite as a slow-release fertilizer and controlling pests. Moreover, this review discusses the integration of natural zeolite with chemical-based wastes from livestock with nitrogen demand for cultivation is explained as a part of the idea of one-system-integrated farm and livestock. Storage and processing of agricultural products could be more efficient with the utilization of zeolite in drying, storage, processing, and product preservation unit operations. Sucrose crystallization, catalytic reaction inulin to fructose, pinene isomerization and glycerol biodiesel by-product conversion is discussed in this review. As in general, zeolite porosity, topology, silicon to aluminum ratio, and acidity properties become an important factor in catalytic reactions to convert agricultural products into beneficial chemical substances.

Keywords: *zeolite; sustainable agricultural intensification; catalysts; agroindustry*

1. INTRODUCTION

According to the Indonesian Central Bureau of Statistic in 2015, Indonesia has a total population of 255,182,144 (BPS, 2015). The number will be estimated to grow nearly 300 million people in 2035 (BPS, 2013). This rapid growth shall be equivalently followed by the number of agricultural productions to guarantee future food national security. On the contrary, the total area of agricultural land was reduced and become one of the biggest threats to agricultural stocks. Agriculture intensification is one way to increase crops productivity. The common practices of intensification are by modified-cultivation, fertilization by using synthetic fertilizers, seeds sortation, pest, and weed control by using pesticides and effective irrigation upon the limited land area.

Despite the agricultural intensification, processing of agricultural derivatives was also required to increase economic value and able to produce beneficial industrial outcome both of bulk and fine chemicals. Agroindustry is an industry that yields a variety of products which mainly composed of cattle and crops (Sukardi, 2011). Agroindustry activities involve many processes like physical and chemical treatment for improving the added value of agriculture products. Some examples of physical treatment in agroindustry are farm product size classification, cleaning process, packaging and drying whereas chemical treatment in agroindustry could be found on corn-starch conversion into fructose syrup by an enzymatic scheme (Keim et al., 2016). Agroindustry activities that implied surround the land area could create new jobs for people who lived around and thus raising the amount of income while also reducing the tendency of urbanization.

Agrochemicals, i.e. chemical fertilizer and pesticide have been applying for agriculture intensification in Indonesia since the 1960s. The utilization of agrochemicals were successfully increased crop yields. However, chemical fertilizer gives negative impacts to the environment such as soil deterioration, greenhouse gas emissions, and water contamination (Díez et al., 2018; Uphoff et al., 2016; Y. Wang et al., 2018). Another concern is regarding the sustainability of chemical fertilizer. For example, urea one of well-known chemical fertilizer is produced from nitrogen in the air and hydrogen which is synthesized through steam reforming process from natural gas and water. The natural gas is a non-renewable resource which is depleting by the time. Urea is also difficult to be absorbed by the soil lead to ineffective utilization of urea dispersed on the farm (Souza et al., 2018). This caused water contamination and greenhouse gas emissions. Controlling pest and weeds by pesticides has multiplied crop harvests. Unfortunately, pesticide causes negative health effects (Papadakis et al., 2015). Long term exposure to pesticides causes serious health problems such as cancer, nerve system abnormalities, and genetic damage (Li, 2018). Hence, there is an urge to substitute agrochemicals with sustainable, eco-friendly, and no adverse health effects.

Zeolite has the potency to be used within the agricultural intensification processes and agroindustry. Zeolite is a chemical compound mainly composed by alumina-silicate with oxygen bonded and repeatedly connected each other to make a channel and micropore cage that could be filled by metal like sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) as compensation of electron excess from aluminium. Originality zeolite could be categorized into two parts, i.e., natural and synthetic zeolites. Application of natural zeolite has been widely known for its agricultural purposes like soil improvements, fertilizing agent and medium for planting (de Campos Bernardi et al., 2013; Frederick A. Mumpton, 1999). On the other hand, synthetic zeolite usually used as a catalyst in the industrial commercial application such as refinery factory, petrochemical plant and adsorption agent for gas treatment industry (Primo et al., 2014). The authors have never found the commercial application of synthetic zeolite as catalysts in agroindustry. Nonetheless, the research of synthetic zeolite for agricultural intensification and agroindustry application was reported in the open literature (Abasaeed et al., 1999; Abasaeed et al., 1995; De Smedt et al., 2015; Oh et al., 2017; Smedt, 2016).

The review of zeolites for agriculture and aquaculture application in general perspectives are available in the literature (Colella, 2005; Ghasemi et al., 2016; Kusdarto, 2008; Ramesh et al., 2011). However, the application of zeolites for catalytic reaction in agroindustry and agricultural intensification is rarely found. This review discusses recent development both of natural and synthetic zeolites application for agricultural intensification and catalytic reaction in agroindustry. Furthermore, the study of its potency in adding economic value from agricultural derivatives by catalytic reactions in agroindustry is also explained.

2. ZEOLITE

Zeolite is a porous material in which consist of channels and cages with the size between 3-20 Å. Zeolite firstly discovered lies beneath earth thus called as a "natural zeolite". Cronstedt was the first researcher who has studied the zeolite material from Sweden and Iceland in 1756 (Colella et al., 2007). Zeolite in terminology means 'stone that generates steam'. The name was given due to zeolite properties which could be used as a water trap. After 200 years of the natural zeolite discovery, Barrer success to synthesize zeolite in the laboratory for the first time (Flanigen, 2001). Until now, there are 234 different types of zeolite framework with each unique name (Colella et al., 2014). The comparison between natural zeolite and synthetic zeolites is presented in Table 1.

Table 1. Differences between natural and synthetic zeolites

Properties	Natural zeolites	Synthetic zeolites	Ref.
Price	0.04-0.25 USD/kg	10-20 USD/kg	(Groen et al., 2007; Kusdarto, 2008; Verboekend et al., 2013)
Crystallinity	Low	High	(Kurniawan, Muraza, et al., 2018)
Surface area	10-100 m^2/g	Up to 3700 m^2/g	(Bakare et al., 2018; First et al., 2011; Kurniawan, Muraza, et al., 2018)
Impurities	High	Low	(Kurniawan, Muraza, et al., 2018; Nasser et al., 2016)
Number of frameworks	44	234	(Colella et al., 2014; http://europe.iza-structure.org/IZA-SC/ftc_table.php)
Formation/ synthesis time	Few days-million years	Few days	(Iijima, 1980)
Si/Al	low	Low to high	(Bakare et al., 2018; Iijima, 1980)

Natural zeolites are low-cost minerals and abundant. In contrast, synthetic zeolites are expensive as presented in Table 1. The disadvantages of natural zeolites are high impurities, low crystallinity and surface area, and non-consistent composition. The chemical compound of natural zeolites varies depending on their location, it is possible to find different types on the same deposit site (Colella, 2005). Synthetic zeolites have many advantages including fewer impurities, high crystallinity, higher total area surface, and good consistency rather than the natural ones. Therefore, commercial catalytic reactions more likely to applied using synthetic zeolites than natural zeolites. So far, industries demand a catalyst with the stringent specification in which only could be fulfilled by synthetic zeolites.

2.1 Natural Zeolite

The International Mineralogical Association (IMA) defines natural zeolite as crystalline material consisted of tetrahedral oxygen which surrounds one cation (Coombs et al., 1997). Zeolite framework contained a void space composed by channels and cages. Usually, it filled by a water molecule or any cation that easy to exchange. On the hydrated phase, dehydration occurs at temperature below 400 ^oC and reversible. The framework could also be found interrupted by OH- and F- group which able to substitute a single tetrahedron corner that is not shared with its verge.

Mordenite and clinoptilolite are the two most frequently natural zeolites found in Indonesia. The natural zeolites rarely occur in a pure phase of the zeolite framework. (Kurniawan et al., 2018) Zeolite from Klaten was reported as a mixture of mordenite and clinoptilolite. In accordance, zeolite from Pacitan, East Java was identified as mordenite (Kusuma et al., 2013). Zeolite from Bayah, West Java was reported to contain clinoptilolite phase (Mahdi et al., 2016); however other identified that the natural zeolites from Bayah were mordenite (Nuryoto et al., 2017). These facts show that natural zeolites phase is vary even in the same sediment deposit.

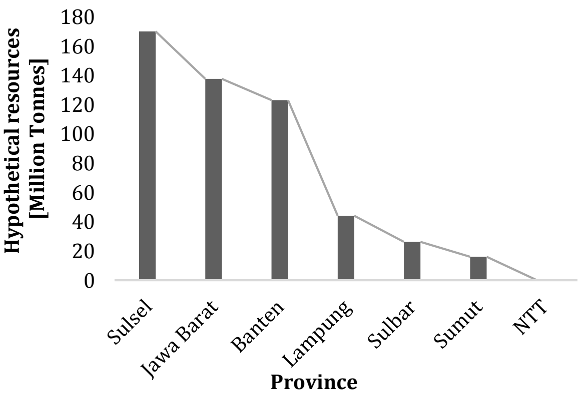


Fig. 1. The hypothetical potency of natural zeolites for several provinces in Indonesia (Kusdarto, 2008).

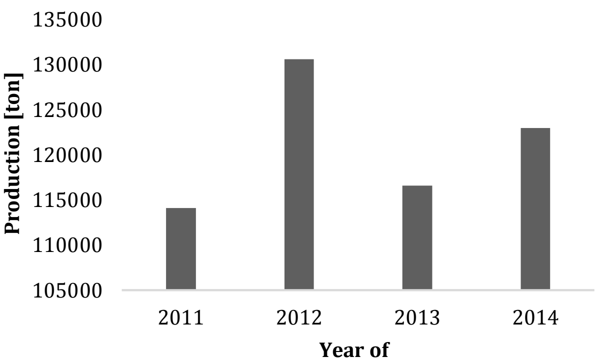


Fig. 2. Natural zeolites production between 2011 – 2014 in Indonesia (https://www.bps.go.id/linkTabelStatis/view/id/1799).

One can see in Figure 1 that natural zeolites potency in Indonesia is enormous. However, production of natural zeolite is still very low (Figure 2) as compared to China who has natural zeolites production 1750000 to 2250000 ton per year (Marantos et al., 2012). Mostly Indonesian natural zeolites are used for soil amendment in palm oil, cacao, and rubber plantation. Some of the Indonesian soil types are peat soils which are notoriously acidic. Hence, the natural zeolites with basic properties due to the high content of Ca^{2+} and K^+ can amend the soil. Those minerals also needed for plant growth. Moreover, the natural zeolites can increase the cation exchange capacity (CEC) which is a measure of cations (K^+, NH^{4+} Ca^{2+}, etc.) amount can be retained on soil surfaces. Some farmers also use natural zeolites in shrimp pond to reduce ammonium content. However, the practice of using natural zeolites for removing ammonium in brackish water was reported ineffective (Zhou et al., 2014). In industrial application, natural zeolites are utilized in wastewater treatment of factories to remove the dye in the textile industry (Saputra et al., 2017).

2.2 Synthetic Zeolites

Zeolite could be synthesized by the hydrothermal process under controlled operating conditions and using chemical compounds with a specified proportion to build its unique framework. The synthetic zeolites provide more zeolite frameworks as compared to the zeolites occurring in nature. Hence, the application of synthetic zeolites wider for sorbent and catalytic reaction than the natural zeolites. Moreover, synthetic zeolites are produced within a relatively short period of time. Recently, microwave assisted zeolite synthesis was investigated which showed that zeolites could be synthesized faster as compared to the convection heat transfer mechanism (Khalil et al., 2016).

Synthetic zeolite currently plays an important role in the conversion of chemical products from fossil fuel such as petroleum, coal and natural gas. Zeolite mostly used as a catalyst in the refinery and petrochemical industries (Primo et al., 2014). The number of zeolite market reached USD 1.8 Billion in 2004, mostly for fluid catalytic cracking (FCC). For example, zeolite Y is utilized for oil cracking. Main products of the FCC process are alkane, alkene, cycloalkane in which beneficial for fuel transportation and raw material of the petrochemical industry. Another example is isomerization reaction of straight-chained alkane to produce iso-alkane using commercial mordenite zeolite as fuel enhancement to get higher octane number, a raw material for methyl tert-butyl ether as anti-knocking and also become a substitute of chlorofluorocarbons that harm the ozone layer (Corma et al., 1995; Hidalgo et al., 2014).

In the petrochemical industry, synthetic zeolites are used as a catalyst or catalyst support in aromatic production like benzene, toluene and xylene and olefins such as ethylene and propylene. Olefins are important raw material for polyethylene and polypropylene production. The commercial zeolite that has been established for this process is ZSM-5 that convert propane, butane, and naphtha into olefins (Kubička et al., 2015; Vermeiren et al., 2009). Research and development of zeolite as a catalyst for olefin production particularly propylene from naphtha is still growing due to its future high demand. Today, olefin production from naphtha without catalyst operates at high temperature (ca. 850 ^oC) (Seifzadeh Haghighi et al., 2013). Using zeolite as a catalyst like ZSM-5, reaction temperature could be reduced to less than 650 ^oC with high conversion of propylene and ethylene (Konno et al., 2012).

3. ZEOLITE FOR SUSTAINABLE INTENSIFICATION

3.1 Slow Release Fertilizer

The utilization of synthetic fertilizer like urea ($CO(NH_2)_2$) had been proven in increasing world food production. However, the ability of the plant to absorb fertilizer is poor as compared to how much fertilizer that had been dispersed on the farm area. The unused synthetic fertilizer further becomes wasted and caused eutrophication which is booming of water plants due to excessive nutrition within the river or lake. The most noticeable effect of eutrophication is the creation of dense blooms of harmful, foul-smelling phytoplankton that decline water clarity and decrease water quality (Chislock et al., 2013).

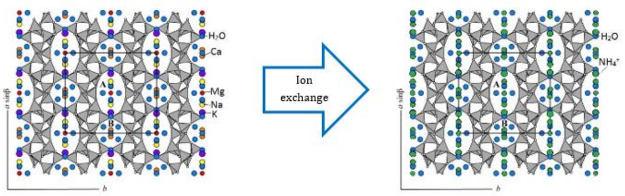


Fig. 3. Schematic of ion exchange on zeolite.

Ammonium (NH_4^+) adsorbed into zeolite porous prevented to form NO_3^- which will prolong releasing ammonium (Figure 3). Decreasing of ammonium conversion to nitrate will reduce nitrogen release into the atmosphere, hence the utilization of urea with zeolite could be more efficient than without using zeolite. According to (Latifah et al., 2017) mixing clinoptilolite with urea can lower urea consumption up to 50% from standard urea consumption per acres on corn plants. This was in agreement with Souza et.al investigation results who developed tablet of urea and clinoptilolite mixture. The tablet dimension is 7 mm of diameter and 4 mm of thickness with a mass within of 150-160 mg. They found that the tablet of urea and clinoptilolite mixture reduced the ammonia volatilization 53% as compared with the tablet of pure urea (Souza et al., 2018). Unfortunately, the tablet has not investigated yet for its effectivity on fertilizing the crops. This high efficiency of fertilizing by using natural clinoptilolite will promote sustainable intensification agriculture.

Zeolite could also be incorporated with other minerals ion such as potassium and magnesium (Mg^{2+}) which are needed by crop plants. In fact, natural zeolites typically found in a various mixture of cations such as potassium, magnesium, and calcium (Kurniawan, Muraza, Hakeem, & Al-Amer, 2017; Frederick A Mumpton, 1985). The potassium is essential for improving crop yield. Zeolite could also adsorb Na^+ which occurs in salty soil and retain the Na^+ inside the pore. For example, natural clinoptilolite was successfully applied to high salinity soil adsorbing Na^+ (Noori et al., 2006). The salty soil contains 0.13 kg NaCl/m^2 added with 0.06 kg natural clinoptilolite per m^2 improve the number of leaf 6 times as compared to salty soil without natural zeolite. The natural zeolite was not only acting as a scavenger of NaCl but also as buffer soil pH level.

3.2 Agriculture Waste Degradation Via Anaerobic Path using Zeolite

Integration of agriculture and livestock is important to be applied in a rural area, particularly when the fertilizer is expensive. It will impact and give many benefits, especially for the land worker and farmer. The closed-cycle of biomass on the farming area could be applied by the anaerobic process using zeolites to produce fertilizer as well as biogas (Figure 4). Agriculture waste from the crop is a good source of raw material for livestock feed such as rice straw, corn stalk, palm oil fond, sweet potato leaves. However, the feed nutritive value could be improved by applying a simple method through ensiling agriculture waste (Oladosu et al., 2016). Another purpose could be found on small industries like wasted of tofu production, a starch by-product from corn flour, wasted-coconut from virgin coconut oil factory, rice bran of rice grinding process, rotten fish processing, broth concentrate yielded from animal bones on the slaughterhouse.

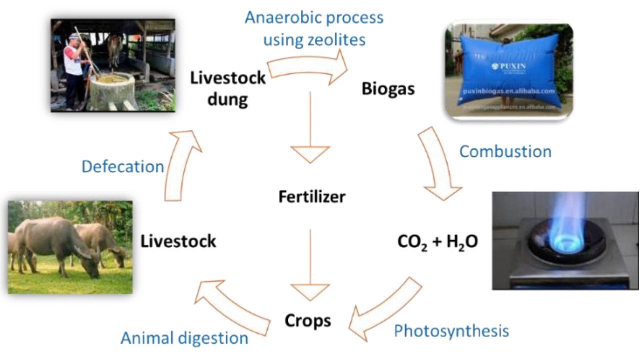


Fig. 4. Closed-cycle sewage utilization around farm area using zeolite in the anaerobic process.

Cattle dung which converted into biogas by an anaerobic process. The wasted by-product from these processes could also be maintained as organic fertilizer for plants. Zeolite has great potential to be applied in the anaerobic reactor to adsorb ammonium and becomes a host for microorganisms to prevent carryover by liquid flow within the reactor (Liu et al., 2015; Montalvo et al., 2005; Wijesinghe et al., 2018). Saturated zeolite with a high content of ammonium could not be exploited as slow release agent fertilizer. Biogas with methane content 48% and carbon dioxide 49% can be purified into biomethane with methane content ≥ 98% by using vacuum swing adsorption (Jiang et al., 2018; Petracchini et al., 2017).

(Parajuli et al., 2018) proposed a new system of integration mixed crop-livestock system by using a green biorefinery and biogas conversion system and studied through life cycle analysis approach. The green biorefinery system basically converts the raw materials of biomass i.e., grass-clover into feed protein and fodder silage whilst the decanted juice and manure processed into biogas in the anaerobic digester. The new system reduces the greenhouse gasses emissions significantly 19.6 kg CO_2 eq for global warming potential; 0.11 kg PO_4 eq for eutrophication, -129 MJ eq for non-renewable energy use and -3.9 comparative toxicity units for potential freshwater ecotoxicity. Addition of zeolite in the anaerobic system may improve the yield of biogas in the integration mixed crop-livestock system by using green biorefinery and biogas conversion. The integration system combined the production of food, feed, and fuels in the farming area resulted in reduced environmental impacts as compared to the livestock production system without biogas processing and green biorefinery systems.

3.3 Zeolites for Controlling Pests

De Smedt et. al. (De Smedt et al., 2015; Smedt, 2016) investigated the application of synthetic zeolites for crop protection. The framework of synthetic zeolite investigated was zeolite Na-LTA. Zeolites sprayed on the leaves to form layers which is useful as particle films to protect the crop from insects and various diseases. Zeolites with their large pore and high surface area are able to adsorb carbon dioxide and reduce the heat stress on plant leaves. Those features are beneficial for plants as a leaf coating product. The properties of protecting the plant from fungal and insects are by their water sorption capacity and small particle size. Zeolite with high aluminium content is a hydrophilic material which is suitable to capture and store water in their pores and cages. Hence, it prevented arthropod influxes, reduced oviposition rate and decreased the number of insects on the leaves.

Natural zeolites could also be applied as inert dust for controlling insecticides in a storage bin. Inert dust is an inert dry powder that used in the storage bin of grain to control the pest such as clay, paddy husk ash, and wood ash (Subramanyam et al., 2000). Natural zeolites are more environmentally friendly as compared with the synthetic insecticides. (Rumbos et al., 2016) studied the effectivity of natural zeolites from various places, i.e., Turkey, Slovakia, and Bulgaria for controlling *Sitophilus oryzae*, *Tribolium confusum* and *Oryzaephilus surinamensis* in wheat. The *Oryzaephilus surinamensis* was the most affected insects by the zeolites with mortality up to 8% after 2 days exposure of 1000 ppm dose. They also studied the effect of particle size (0-50, 0-150, and 0-500 μm). They found that the small particle size was more effective for controlling the insects. Recently, (Kavallieratos et al., 2018) investigated the efficacy of the same natural zeolites used by Rumbos et.al for protecting grain wheat from mite species in the storage. The natural zeolites showed high mortality up to 26% of the mite species after 2 days exposure with 1000 ppm dose. Longer time of zeolites exposure might be needed to reach 100% mortality of insects.

4. ZEOLITE FOR AGROINDUSTRY

4.1 Drying Promotor

Zeolite has an ability to store water molecules within its porous geometry. Hence, zeolite is potentially applied as desiccant. Water absorption capacity depends on the zeolite framework, porosity, surface area and its chemical composition (Tatlier et al., 2018). The ratio of Si/Al also influenced the capacity of water adsorption in zeolite pores and cages. Low Si/Al ratio favor water adsorption, on the other hand, high Si/Al ratio reduce the ability of zeolite to adsorb water. Utilization of zeolite could increase the efficiency of the drying system in the dryer machine (Djaeni et al., 2007).

4.2 Sucrose Crystallization

The selectivity of zeolite which provided by different shape and molecule sizeable to separate sucrose molecules from water (Lee et al., 2012). (Fornefett et al., 2016) reported that zeolite Y with high Si/Al ratio prefer to adsorb sucrose than water. Then, sucrose was released from the zeolite pore by using ethanol. Hydrophobic zeolite-Y was applied to adsorb sucrose from molasses. They also reported that the low Si/Al a ratio which is hydrophilic could adsorb sucrose in ethanol solvent. However, different procedure was applied to release the sucrose from zeolite pore. They used water to desorb sucrose instead of ethanol. Low Si/Al ratio is typical of natural zeolites. One can use acid treatment to decrease aluminum content in a zeolite (Kurniawan et al., 2017).

4.3 Packaging of Intense Fruit Fragrance

Zeolites have a unique feature which called as shape selectivity. Molecules with certain size and shape could retain in the pore of zeolites while other molecules can pass the pores. (Keshavarzi et al., 2015) reported that ZSM-5 could be mixed with nano-cellulose fibrils to produce an active packaging which effectively removed odor from rich the fruits having strong aroma such as durian. It is found that the volatile odors molecules from durian were ethanethiol and propanethiol which were adsorbed in pore of ZSM-5. Hence, the concentration of ethanethiol and propanethiol that passed the zeolite packaging barrier was under human sensory detection.

5. ZEOLITE FOR CATALYSTS IN AGROINDUSTRY

In this section, the application of zeolites in agroindustry as a catalyst to convert product and by-product of agriculture crop into more valuable substances is discussed.

5.1 Inulin Conversion into Fructose

Inulin is abundant in several root-plants such as dahlia, chicory, and Jerusalem artichoke. Dahlia able to grow in Indonesia, especially for decorative plants. Catalytic conversion technology of inulin to fructose gains the new opportunity of Dahlia's research and development. (Abasaeed et al., 1995) had been studied modernite zeolite that could convert inulin which consisted of fructose monomer to fructose molecules. Modernite zeolite has advantages like easy to separate with main products and avoid to generate by-products like hydroxymethylfurfural (HMF). There were also reports of various type of zeolites framework which have potency for converting inulin into fructose as a presenter in Table 2.

Table 2. Inulin conversion into fructose over zeolites catalysts.

Inulin sources	Catalyst	BET Surface Area* (m^2/g)	Si/Al	conversion	Type of reactor (Temperature)	Ref.
Artichoke Jerusalem *(Helianthus tuberosus)*	Mordenite (H-MOR)	480	8	95%	Batch Reactor (130 °C)	(Abasaeed et al., 1995)
Computational Simulation	Mordenite (H-MOR)	480	8	100%	Fluidized Bed Reactor (130 °C)	(Abasaeed et al., 1999)
Commercial Inulin (Alfa Aesar)	Ferrierite (H-FER)	364	28	75%	Three-neck rounded flask (92 °C)	(Oh et al., 2017)
Commercial Inulin (Alfa Aesar)	Mordenite framework inverted (H-MFI)	466	40	80%	Three-neck rounded flask (92 °C)	(Oh et al., 2017)
Commercial Inulin (Alfa Aesar)	Beta (H-BEA)	612	19	78%	Three-neck rounded flask (92 °C)	(Oh et al., 2017)
Commercial Inulin (Alfa Aesar)	Mordenite (H-MOR)	552	45	80%	Three-neck rounded flask (92 °C)	(Oh et al., 2017)
Commercial Inulin (Alfa Aesar)	Mobil Composition of Matter-tWenty-tWo (MWW)	597	20	78%	Three-neck rounded flask (92 °C)	(Oh et al., 2017)
Commercial Inulin (Alfa Aesar)	Faujasite (FAU)	632	40	82%	Three-neck rounded flask (92 °C)	(Oh et al., 2017)
Commercial Inulin (Alfa Aesar)	pillared MFI (PMFI)	530	70	76%	Three-neck rounded flask (92 °C)	(Oh et al., 2017)
Commercial Inulin (Alfa Aesar)	pillared MWW (PMWW)	694	30	80%	Three-neck rounded flask (92 °C)	(Oh et al., 2017)

* *Brunauer–Emmett–Teller*

The conversion of inulin over zeolites were affected by the temperature as presented in Table 2. High temperature favoured the high conversion of inulin over zeolite mordenite. The topology of zeolite had a small effect on the inulin conversion. FAU showed the highest conversion among the zeolites studied because has large pore zeolite and 3D pore structure. However, the selectivity of inulin into fructose, sucrose, and glucose was affected significantly by the pore size of zeolite. Large pore zeolites like BEA and FAU exhibited pore mouth catalysis which acted on the cleavage of glucosyl-fructosyl bonds as indicated by increasing of glucose amount. Whereas, the small pore zeolites did not show the pore mouth catalysis activity (Oh et al., 2017).

5.2 Sucrose Conversion into Glucose and Fructose

Indonesia has many sucrose sources trees such as sugar cane, sugar palm, coconuts, doub palm (*Borassus flabellifer*) and nipa palm (*Nypa fruticans*) (Kurniawan, Jayanudin, et al., 2018). Sucrose could be converted to inverted sugar like fructose and glucose which further serve as a food sweetener in fruit jams and corn syrup. The conversion of sucrose into invert sugar commercially performed over the enzymatic process. However, the enzyme that used in the process has some disadvantaged such as producing waste, difficulty in separation and reused the enzyme from the product and low thermal stability (Pito et al., 2012). Heterogeneous catalysts like zeolites offer advantages over the enzymatic process i.e., easiness in catalyst separation with the products and high thermal stability.

Moreau et al. (2000) studied the effect of temperature (75-100 °C) and time of reaction (0-150 min) on the hydrolysis of sucrose over faujasite (FAU) zeolite. It was observed that the sucrose converted almost 100% into fructose, glucose, and 5-hydroxymethylfurfural at temperature 100 °C. However, the concentration of by-product 5-hydroxymethylfurfural was increase at high temperature. Similarly, the longer time of reaction favoured selectivity to 5-hydroxymethylfurfural. The deactivation of the catalyst was observed during the hydrolysis process. The catalyst was easily regenerated after 7 days period by using simple thermal treatment. Moreover, zeolite also reduced the color pigmentation of the invert sugar (Moreau et al., 2000).

5.3 Isomerization of Pinene

Pine (*Pinus merkusii*) is a plant of gum sources that produce *gondorukem* (*Resina colophonium*) and turpentine. Turpentine mainly consisted of α-pinene molecule. One of Indonesia's national-owned enterprises (Perum Perhutani) built a derivate factory to process pine extracts such as resin and turpentine. The process using phosphate acid as a catalyst to manufacture derivative products like glycerol esther, α-pinene, β-pinene, d-limonene, α-terpineol, cineol dan diterpene. Isomerization of α-pinene and its oxides is important for the specialized-chemical industry to generate high-value components such as camphene, limonene, campholenic aldehyde (CPA) that are widely used of fragrance and flavour for dirt cleanser, cosmetics, perfume, food additives and also pharmacies (Figure 5) (Climent, Corma, & Iborra, 2010). Isomerization of turpentine also could be established by using zeolite catalysts such as H-beta, MCM – 22 and USY types (Ma et al., 2017).

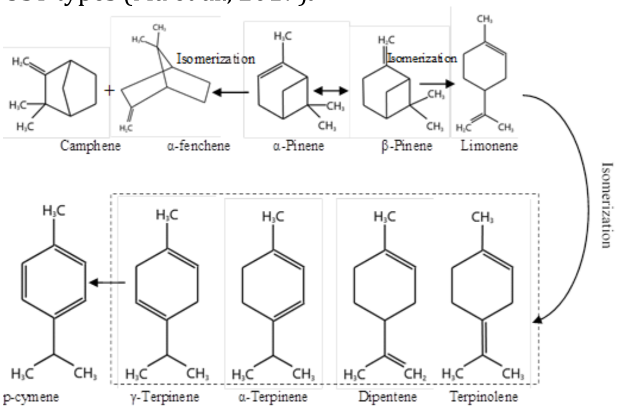


Fig. 5. Chemical derivatives from isomerization of pinene (Climent et al., 2010).

Lemongrass (*Java citronella*) contained an important specialized-chemical compound named citronella (Figure 6). These molecules could be converted into isopulegol by cyclization. Isopulegol is an intermediate product of menthol synthesis that could also be used as raw material on fragrance and perfume industries. The total annual world production of menthol in 2007 reaches 20,000 tons, making menthol is one of the world most important chemicals. Menthol easily found on pharmacies, toothpaste, gums, cosmetics and also convection industries. Cyclization of citronella using zirconia-zeolite beta exhibits an isopulegol product (Yongzhong et al., 2005). Zeolite with high porosity like zeolite beta with high Brønsted acid sites tended to initiate cyclization rather than zeolite with small porosity and low Brønsted acid sites (Mäki-Arvela et al., 2004; Mertens et al., 2006; Plößer et al., 2014).

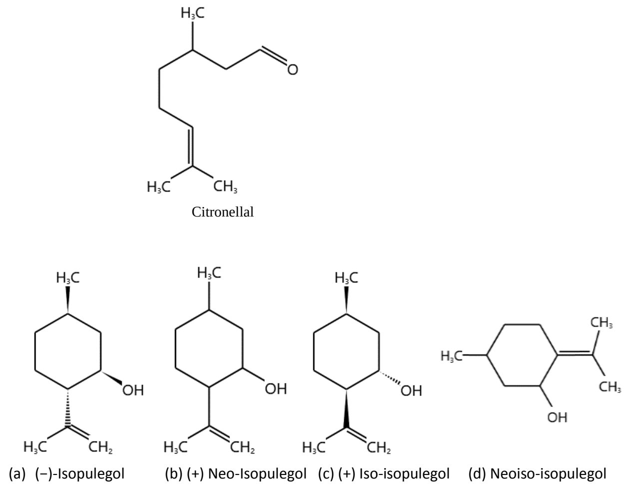


Fig. 6. Cyclization of citronella into isopulegol (Yongzhong et al., 2005).

5.4 Glycerol Ketalization

Glycerol is polyalcohol with chemical composition of $C_3H_5(OH)_3$. Around 10% of biodiesel production capacity is converted into glycerol as a by-product of transesterification reaction (Ozorio et al., 2012). Glycerol could be straightforwardly processed into high economic value derivatives like solketal (Figure 7). This substance is potentially utilized as a gasoline additive to increase octane number and reducing gum content.

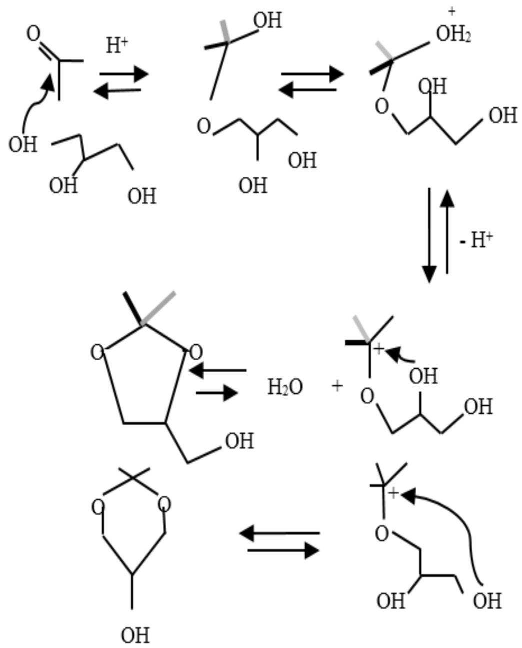
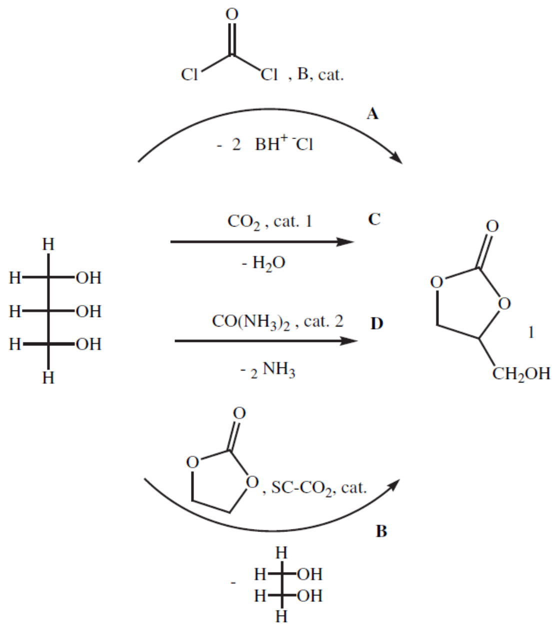


Fig. 7. Acetylization of glycerol and acetone to solketal (Nuryoto et al., 2017).

Solketal could be synthesized by using catalyst contains H^+ groups involving synthetic zeolite (zeolite beta – zeolyst CP814E), zeolite X and zeolite Y (Aldrich) [amberlyst 15, titanium oxide, zirconia, and natural zeolites [83-87]. High porosity and superior surface area (~60%) tended to established good solketal product selectivity (~30%) and high glycerol conversion (Nuryoto et al., 2017).

Glycerol could also be processed to glycerol carbonate and triacetin (Climent et al., 2010; Takagaki et al., 2010). Triacetin is used as diesel oil additives and glycerol carbonate is used as surfactant, solvent and intermediate product of synthetic polymerization. Mechanism and equilibrium reaction of glycerol carbonization into carbonate process is described in Figure 8 as follows (Casas et al., 2010; Rao et al., 2011).



(Route A: Glycerol + Phosgene;
Route B: Glycerol + other chemicals;
Route C: Route + Carbon Dioxide;
Route D: Glycerol + Urea)

Fig. 8. Glycerol carbonization into carbonate compounds (Dibenedetto et al., 2011).

The stepwise reactions of glycerol conversion into triacetine is presented in Figure 9. Gelosa et al (Gelosa et al., 2003) observations establish 3 equilibrium reaction stages of triacetin: Step 1: Conversion of glycerol to monoacetine; Step 2: Conversion monoacetine to diacetine and Step 3: Conversion diacetine to triacetine. Simplification of triacetine equilibrium reaction define as follows:

glycerol + acetic acid ↔ monoacetine + water (1)
monoacetine + acetic acid ↔ diacetine + water (2)
diacetine + acetic acid ↔ triacetine + water (3)

Fig. 9. The reactions of glycerol into triacetine.

Solketal, glycerol carbonate, and triacetin could be synthesized using a catalyst with H^+ groups. Zeolite synthetic such as zeolite beta (zeolyst C814E), zeolite X and zeolite Y, amberlyst 15, titanium oxide, zirconia and natural zeolites (Nuryoto et al., 2017). Meanwhile, triacetine could be synthesized by using Amberlyst-15 and sulfate acid as their catalyst agent (Gelosa et al., 2003), whereas natural zeolite had been experimented for triacetine production and show promising yield. A common catalyst to exhibit glycerol carbonate is Indion-225-Na in which Na^+ groups within resin could be exchanged with H^+ groups using the solution of strong acid natural zeolite (Mahdi et al., 2016) and lanthanum oxide (L. Wang et al., 2011). Natural zeolite proves to generate a good result of glycerol conversion to triacetine, solketalthe and carbonate glycerol. About 60% glycerol was converted to solketal with selectivity up to 30% [40] whereas more than 50% of triacetin raw material could be processed converted into glycerol carbonate (Mahdi et al., 2016; Nuryoto et al., 2017). It has been shown that natural zeolite was potential to be developed although it requires more comprehensive research to establish the standard theory of reaction.

6. CONCLUSION & FUTURE PROSPECTIVE

Natural zeolites and synthetic zeolites might have more important roles in agriculture and agroindustry sectors in the future. Natural zeolites with huge deposit throughout the world are potential to be applied in agriculture intensification for slow release fertilizer, controlling pests, and anaerobic process. Moreover, natural zeolites are relatively low-cost minerals that can be used in agroindustry for example in the drying process, grain storage, and packaging of bad smell fruits. There are recent reports that zeolites, particularly synthetic zeolites, are also a promising candidate for agriculture products valorization through catalytic reactions of numerous reactions such as inulin conversion, hydrolysis of sucrose, isomerization of pinene, and ketalization of glycerol. Research and development of zeolites application for other catalytic reactions need to be enhanced because of the high potential of zeolites.

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