*บทความวิชาการ*

# ปริทัศน์ของไอออนิคลิควิดเพื่อเป็นตัวเร่งปฏิกิริยาผลิตไบโอดีเซล

# Review of Ionic Liquid as a Catalyst for Biodiesel Prodution

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## บทคัดย่อ

การประยุกต์ใช้ไอออนิคลิควิด (Ionic liquid) เพื่อผลิตไบโอดีเซลกำลังได้รับความสนใจในด้านการวิจัยและพัฒนาเนื่องจากมีประสิทธิภาพสูงและคุณสมบัติที่เป็นมิตรต่อสิ่งแวดล้อม โดยไอออนิคลิควิดทำหน้าที่เป็นตัวทำละลาย ตัวทำละลายร่วม ตัวเร่งปฏิกิริยา หรือตัวสนับสนุนตัวเร่งปฏิกิริยาในปฏิกิริยาทรานเอสเตอริฟิเคชั่น (transesterification) และเอสเตอริฟิเคชั่น (esterification) ซึ่งได้มีการศึกษาการประยุกต์ใช้ไอออนิคลิควิดในปฏิกิริยาต่าง ๆและติดตามประสิทธิภาพในการทำงานของไอออนิคลิควิด และพบว่าไอออนิคลิควิดนั้นสามารถลดข้อจำกัดของกระบวนการผลิตไบโอดีเซลที่มีในการผลิตไบโอดีเซลด้วยวิธีการทั่วไปที่มี กรด เบส หรือเอนไซม์เป็นตัวเร่งปฏิกิริยา เพราะไอออนิคลิควิดสามารถปรับปรุงคุณสมบัติตามที่ต้องการด้วยการดัดแปลงโครงสร้างบางส่วนของแอนไอออน (anion) และแคทไอออน (cation) นอกจากนี้ไอออนิคลิควิดยังสามารถนำกลับมาใช้ใหม่ได้ ซึ่งช่วยลดค่าใช้จ่ายในกระบวนการผลิตไบโอดีเซล

**คำสำคัญ**: ไอออนิคลิควิด ไบโอดีเซล ตัวทำละลาย ตัวเร่งปฏิกิริยา

## Abstract

Applications of ionic liquids (ILs) for biodiesel production attract more interest from the research and development sector because of their high environmentally and environmental friendly properties. IL's play multiple roles as solvent, co-solvent, catalyst, or catalyst support in transesterification and esterification. In this study, their functions and efficiencies for biodiesel production are described. IL performance potentially overcomes some limitations of conventional process that used base, acid, or enzyme as a catalyst because its chemical structure could be tailor-made designed and modified by changing different anion and cation. Lastly, in this study the recycle methods of IL in the process are also presented to reduce the high cost of IL for biodiesel production.

**Keyword**: Ionic liquid, Biodiesel, Solvent, Catalyst

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## Introduction

Chemical process synthesis requires utilization of a certain type of solvent that involves in the reaction to generate a desired product. Many types of commercial solvents are available and extensively utilized in industries in a large amount. Most types of organic solvents are considered to be harmful, and lead to serious hazard when they are exposed to human and/or environment. Lately the interest on the shifting from conventional solvent to ionic liquid (IL) is growing as it is considered to be a promising green solvent due to its non-volatile, non-flammable properties (1)

The main difference between IL and conventional solvent is the vapour pressure. Vapour pressure of IL can be negligible and its property is adjustable for various purposes. ILs are applicable in catalytic reactions, especially, for a reaction that operates at extreme temperature because of their thermal stability, ionic conductivity, electrochemical property, miscibility, and polarity (2). The design of IL is challenging due to its high viscosity and density that is needed to be improved prior to the application in any process. The properties of ILs (density, viscosity, melting point, refractive index, and polarity) can be modified by changing their chemical structures in cation, anion, and/or alkyl chain (Figure 1).

ILs are efficient compounds using in many processes, particularly biomass pretreatment (3). ILs, especially imidazolium and pyridinium derivatives, could be employed in the pretreatment of lignocellulose feedstocks before hydrolysis reaction to promote the release of sugar for fermentation (4). Meanwhile, the use of IL in biodiesel production is recognized as catalyst for transesterification process, solvent, or catalyst support (5). Combination of IL and heterogeneous catalyst performs high activity and stability in the transesterification process. On the other hand, combination of IL with enzyme prevents methanol deactivation of enzyme and enhances the contact between substrate and catalyst by increasing of surface area of catalyst when it is used as catalyst support (6).

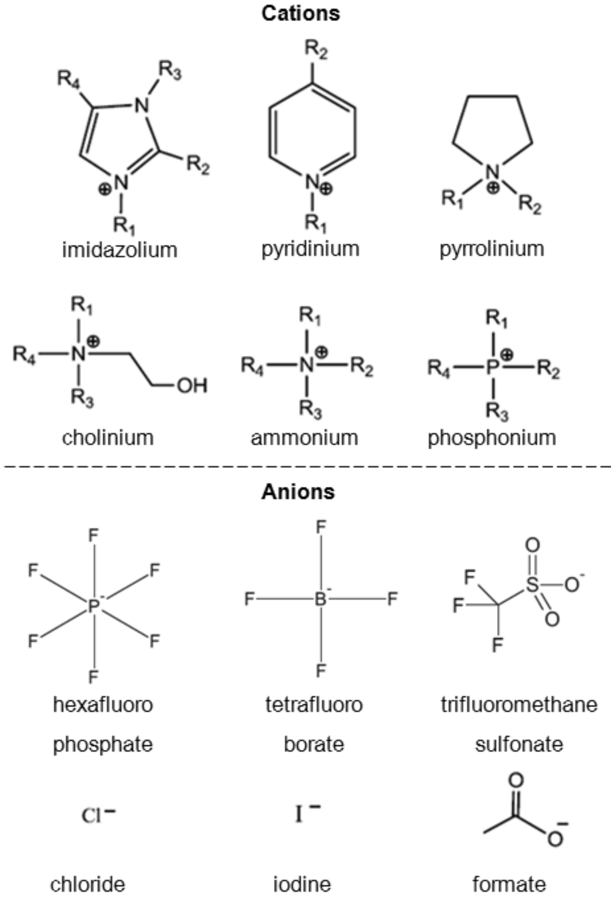

**Figure 1.** Cations and Anions of ionic liquids.

## Acidic and basic ILs function as catalysts in biodiesel synthesis

Similarly to the conventional biodiesel synthesis (Figure 2), acidic IL or basic IL play their roles as regular acid or base catalysts. The acidic IL behaves similarly like the conventional acid catalyst in biodiesel production and it is suitable for feedstocks that contain high Free Fatty Acid (FFA) contents (7). In solid acid catalyst, the esterification occurs when a carbonyl carbon group of a triglyceride/FFA is protonated. Then a nucleophilic carbonium is attacked by an alcohol to form a tetrahydral intermediate, which further forms the Fatty Acid Methyl Ester (FAME) (8). In the transesterification, a proton is attached to the a carbonyl group of a triglyceride. And an alcohol attacks a carbocation to construct a tetrahydral intermediate that later breaks down to form FAME via proton mitigation.

The basic IL catalyst is similar to the conventional basic catalyst, which $OH^-$ takes $H^+$ atom and converts methanol to $CH_3O^-$ (methoxide), and then binds with the imidazolium cation of IL. A carbonyl group of triglyceride is attacked by $CH_3O^-$, to form a tetrahydral intermediate and re-arranges proton to produce FAME or biodiesel (8). It is observed that several basic IL catalysts in transesterification has high catalytic activities and produced the highest yield up to 95% (9).

Both acidic IL and basic IL are able to be recovered and reused for around 5 to 7 times without any significant decreasing on the catalytic activity to the biodiesel yield. Apparently, the acidic IL shows high catalytic activity at higher temperature, meanwhile basic IL could be operated at milder temperature (10). However, the Brønsted acidic IL can be also operated at mild temperature when it has bigger numbers of acid groups (e.g. 4 acid group) (11).

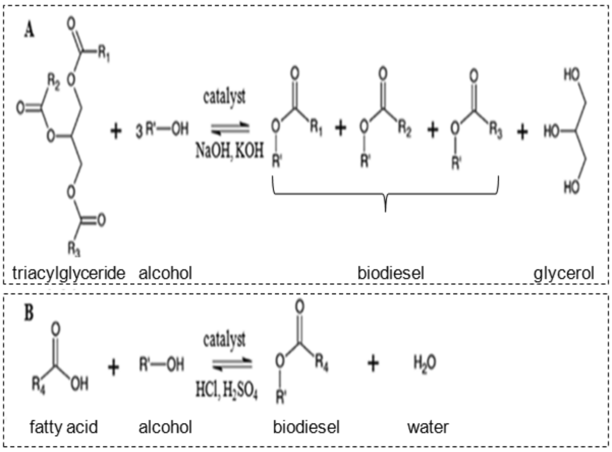

**Figure 2.** Biodiesel production reaction. (A) Transesterification and (B) Esterification (12)

## IL application in the two-step biodiesel production process

The feedstocks for biodiesel production, such as vegetable oil, animal fat, and wasted cooking oil, contain various proportions of triglycerides and FFA that are crucial in determination of the operational condition and selection of the catalysts for the reactions. For example, the saponification reaction is one of the problem that occured in a conventional process when high FFA feedstock is used. To overcome this problem, two-step biodiesel production is applied via esterification reaction first, and then continued with transesterification reaction (12).

The applications of ILs in two-step biodiesel production were previously studied. Ghiaci et al. (2011) observed the effect of Brønsted acidic IL, 1-benzyl-1H-benzimidazole, on biodiesel production from vegetable oil (13). They found that high numbers of Brønsted acidic sites would give high efficiency in the transesterification reaction and resulted in high FAME yield up to 95%. Another Brønsted acidic IL, triethylammonium hydrogensulfate ($Et_3NHSO_4$), was used as the catalyst for biodiesel production from crude palm oil (CPO). $Et_3NHSO_4$ is able to convert 82.1% of FFA under high temperature at 170°C for 3 h with 15:1 ratio of methanol:oil. And then transesterification generated 96.9% biodiesel yield where 1.0% KOH was used as catalyst (under 60°C for 50 min with agitation speed of 600 rpm) (7).

Fauzi and Amin (2013) developed the optimized esterification process using 1-butyl-3-methylimidazolium hydrogen sulfate ($BMIMHSO_4$) as the catalyst. The predicted optimal condition for biodiesel production was achieved at temperature 87 °C, methanol:oil ratio of 9:1, catalyst loading of 6%, with retention time for 5.2 h. The obtained yield of methyl oleate and oleic acid conversion reached to 81.8% and 80.4%, respectively (14). Additionally, acidic IL namely $BMIMHSO_4$, butylimidazolium hydrogen sulfate ($BIMHSO_4$), methylimidazolium hydrogen sulfate ($MIMHSO_4$) were used as the catalysts in esterification of waste cooking oil, and then followed by transesterification using alkaline as the catalyst. When using $BMIMHSO_4$, 95.65% of FAMEs with longer alkyl chain were produced at optimal condition of methanol:oil ratio 15:1, 160°C, 1 h, and agitation speed at 600 rpm (15) (Figure 3).

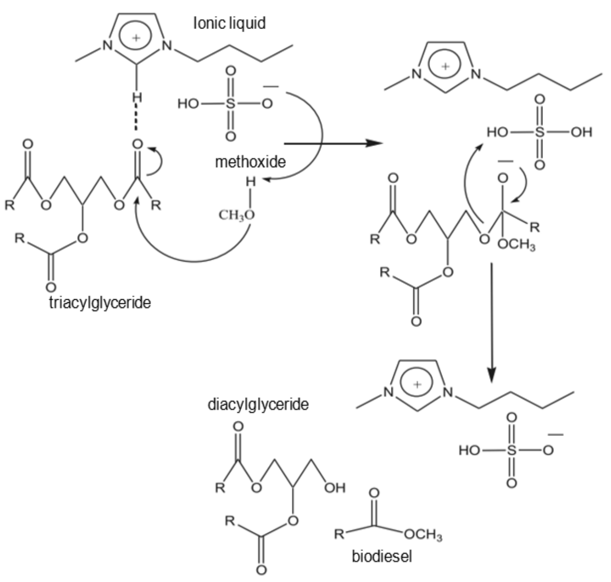

**Figure 3.** Mechanism of the reaction between triglceride and methanol catalyzed by $BMIMHSO_4$ (15)

Although two-step biodiesel production has high efficiency, it leads to complications in the industrial-scale process. The one-step process was developed to reduce this complication by copolymerization between a novel Brønsted acidic polymeric IL, 3-vinyl-1-(4-sulfonic acid) butyl imidazolium hydrogen sulfate ($[SO_3H(CH_2)_3$ VIm]- $[HSO_4]$), and divinylbenzene (DVB) (16). The polymeric IL can be used asa catalyst both in esterification and transesterification simultaneously and produce higher yield (99%) than acidic IL (less than 96%). Since the interaction between water and active site of the catalyst reduces the catalyst efficiency. The polymeric IL has large hydrophobic surface that prevents this interaction. In addition, high stability of polymeric IL enables recycle up to 6 times without significant change in biodiesel yield (16).

## Process improvement for biodiesel production by synthesis of the novel IL

IL poses some pitfalls that could affect the performance of biodiesel production, such as the high cost, high viscosity, catalyst lost, low purity of product (17). One novel IL, deep eutectic solvent (DES), was founded to be useful for the biodiesel production and it was cheaper than conventional IL. DES was synthesized from Choline Chloride·$xZnCl_2$ instead of using imidazolium due to its inexpensive cost and simple preparation technique (18). However, this study obtained only 54.52% of biodiesel yield (at condition methanol to oil ratio 16:1 with 10% catalyst for 72 hours). On the other hand, ammonium based DES, which was prepared by mixing N,N-diethylenethanol ammonium chloride (DEAC) with p-toluenesulfonic acid monohydrate (PTSA) to form DEAC-DES catalyst, was then used for the pretreatment of low grade crude palm oil prior to the transesterification process. It was reported that the remaining FFA in biodiesel was below than 1% indicating the high FAME production during transesterification (19). Using the similar preparation method, Hayyan et al. (2014) continued investigation of esterification of crude palm oil with high content FFA by using choline chloride-DES (ChCl-DES). The result is also similar where 9% of FFA content is reduced to less than 1% and transesterification of this treated crude palm oil obtained 96% of FAME (20).

DES is considered inexpensive, biodegradable and non-toxic. In the reaction, DES mixes with methanol, which allows phases formation with the FAME. The saponification can be reduced due to FAME standing alone in a single phase and has limited interaction with the homogeneous base catalyst. The base catalyst itself dissolves in DES/methanol mixture that causes more interactions and increases the FAME yields up to 98%. The glycerol produced in the reaction can be deposited by DES. However, excess concentration of DES is undesirable due to the competition between glycerol and DES to interact with methanol. Excess amounts of DES to base catalyst lead to reaction inhibition that decrease are FAME production (21).

## IL application in enzymatic catalysis

Over the interest on homogeneous or heterogeneous acid and base catalyst application, the biocatalyst for biodiesel production, for example lipase, is seem to be promising because it provides higher purity of biodiesel, reduces the complexity on glycerol – biodiesel separation, generates zero by-product, consumes less energy, and does not affected by the presence of FFA and water

(22-23). In addition, enzymes are able to precede esterification and transesterification at low temperature, low required amount of methanol or alcohol and no soap formation during the process (24). The challenge of this process is the deactivation of enzyme due to excess amount of methanol. Immobilization of lipase enzyme offers high catalytic activity and stability where the methanol deactivation can be avoided when IL is applied (25). The IL is hydrophilic so it strongly interacts and prevents methanol to bind with the enzyme (26).

These mentioned problems can be solved by three different methods, which are stepwise addition of methanol, acyl acceptor accelerator, and solvent engineering (27). As the solvent, IL could reduce the production of glycerol during biodiesel production due to its low solubility in the IL. However, the low solubility of triglyceride in IL generates low reaction rate. When methanol is additionally mixed to increase the solubility, excess formation of glycerol is observed (28). To minimize this problem, proper amount of methanol is needed to be optimized for enzymatic transesterification.

Novozym 435 is the widely used lipase in the biodiesel production but considered to be high cost due to uncompetitive enzyme price. *Penicillium expansum* lipase (PEL) has been considered to be less expensive enzyme and was investigated in the transesterification of corn oil in the 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF6) and the tert-butanol solvent (29). It was demonstrated that methanol does not affected the PEL activity in this system. IL is useful in enhancing the enzymatic activity during transesterification process because oil and methanol are distributed uniformly with less interaction between methanol and enzyme (29).

The application of IL is not limited to the certain types of feedstocks. Lai et al. (2012) reported on the enzymatic biodiesel production from microalgae oil in ILs (30). The oil was extracted from microalgae in form of lipid and converted by *Penicillium expansum* lipase (PEL) and *Candida antarctica* lipase B (Novozym 435) in BMIMPF6. The IL enhanced the enzymatic activity of PEL and Novozyme 435 when compared to the use of these enzymes in conventional organic solvent. It was revealed that in the IL, PEL and Novozyme 435 catalyzed the reaction and produced up to 90.7% and 86.2% of FAME, respectively. Furthermore, IL is also potential to be used for the lipid extraction due to its property of non-volatility, thermal stability, and synthetic flexibility. IL could produce 1.6 times fold of yield compared to Soxhlet's, and Bligh and Dyer's methods (31).

## IL application in biodiesel production using microwave technique

Microwave heating technique has been widely studied in biodiesel production using various types of the conventional solvents and catalysts (homogeneous, heterogeneous, acid, and base catalyst). Microwave heating system or microwave irradiation enhances the reaction kinetic of the transesterification under short reaction time, and increases biodiesel yield and purity comparing with the conventional heating (32-33).

Dipolar polarization and ionic conduction are two principles that applied in the microwave method. Dipolar polarization occurs when dipoles of molecules align with the electrical field once the microwave introduced into the system. The oscillation of dissolved charged particles that are induced by the microwave is called as ionic conduction (34). Microwave induces the molecular agitation of atoms through dipole rotation or ion migration that promotes collision and molecular attrition (35). Collision and attrition of molecular movement generate heat, which speed up chemical reaction by increasing in the kinetic energy and resulting in short reaction time (35). The polar molecules of vegetable oil, methanol and IL can absorb the microwave energy. In addition, the ionic and polar components in the system help to distribute heat rapidly via conduction and convection (36). In this case, the FAME yield in the microwave heating system is higher than the conventional method where both processes performing in the ILs.

Based on this knowledge, several studies were performed to improve the biodiesel production. Lin et al. (2013) conducted the transesterification of waste cooking oil using IL as a catalyst with microwave heating (37). The 4-allyl-4-methylmorpholin-4-iumbromine ([MorMeA]

[Br]) was combined with NaOH. It was found that the increasing amount of IL with constant amount of NaOH enhanced the biodiesel yield up to 98.1% under microwave heating for 7 min at 70°C with methanol:oil ratio of 9:1. However, higher molar:oil ratio, and longer reaction time cause the decreasing of biodiesel yield due to the excess glycerol production. Heteropolyacid-based (HPA) IL derived from choline-chloride was also tested as heterogeneous catalysts in esterification process under microwave irradiation (38). It was observed that this IL catalyst combined good properties of homogeneous and heterogeneous catalysts, and performed high efficiency up to 97% conversion under microwave heating. Another IL catalyst, 2,3-dimethylimidazolium hydrogen sulfate ($MMBIMHSO_4$), also gives comparable conversion yield of FAME with shorter retention time under the microwave heating comparing with the conventional heating (39).

Interestingly, microwave heating efficiency was evaluated in a system of enzymatic transesterification by Novozyme 435 with several different types of ILs. The optimal yield of transesterification was obtained when using 1-ethyl-3-methy limidazolium hexafluorophosphate (EMIMPF6) as the reaction medium under 60°C. After 6 h of reaction with 6% Novozyme 435 by microwave power at 480 W, the FAME yield reached 92%. However, the agitation of mixture is necessary because of high viscosity of IL. Agitation speed between 50 – 200 rpm could enhances the rate of reaction as interfacial area sufficiently increased (40). Regarding to these studies, the investigation of microwave technique for biodiesel synthesis in IL system is lately gains more interest. This technology also could help to reduce the amount of acid or base catalyst, because the IL promotes the reaction efficiency due to its property to absorb the microwave.

## Ionic liquid recovery

Economical consideration is the drawback of IL as it is relatively expensive compared to the conventional solvent and the catalyst. Therefore, to reduce the process cost, IL recycle is suggested. The recyclability of IL was found up to 6 times without significant reduction of the yield, and no IL degradation was observed (41). Other studies also found that IL catalyst can be reused for 7 times of operation with high yield of biodiesel. However, it can be noticed that at the optimal condition of IL recycle, the declining in biodiesel yield was observed (13). It was explained that the decreasing yield was affected by the remaining amount of glycerol in IL, which decreased the IL activity by the reduction of active sites (37).

Nevertheless, IL enables simple recovery because the process could generates biphasic or triphasic system once the biodiesel synthesis is completed. Several types of ILs were studied to stabilize the lipase enzyme from methanol deactivation in transesterification (42). After the transesterification, triphasic system was formed, which consists of 3 different layers of FAME at the upper layer, glycerol and unconverted methanol in the middle layer, and IL and enzyme in the bottom layer.

Another study employed $MMBIMHSO_4$ as the catalyst in biodiesel production (43). It was reported that the effective recovery of IL can be achieved based on its low melting point property. FAME, methanol, glycerol, and IL were proceeded to the separation process. FAME can be collected by simple decantation, while methanol can be separated under vacuum, which left the glycerol and IL in the system. The IL then was recovered by applying cooling water with temperature below IL melting point to change the phase from liquid to solid. Finally, filtration can be applied to separate glycerol and solid IL.

IL is classified as molten salt, and its recovery as a solvent could be possible by the crystallization (44). Furthermore, the non-volatile and thermal stability property of IL enables the thermal-based separation, such as distillation, to be applied. Super critical $CO_2$ ($scCO_2$) can also be used to separate IL from organic compounds as where organic material is highly soluble in $scCO_2$, while IL is insoluble in $scCO_2$ and settles down to the bottom of the reactor (6, 45) (Figure 4). The adsorption separation of IL using activated carbon is applicable according to the hydrophilic or hydrophobic content of IL. If IL is a highly polar type, the activated carbon should contain high polarity on its surface to occupy the hydrogen bonding between adsorbate and adsorbent (46).

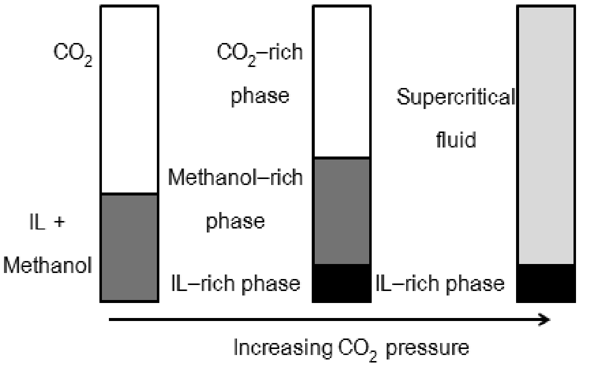

**Figure 4.** Phase behavior of IL recovery process by $scCO_2$ (45)

## Conclusion

The application of IL in biodiesel production can be widely used for many types of feedstocks from 1st to 3rd generation biodiesel. Its property of providing anion and cation as well as modification makes it becomes potential chemical for biodiesel synthesis. The utilization of IL eliminates the limitation of heterogeneous, homogeneous, or biocatalyst. And by merging it with microwave heating, the reaction time can be greatly reduced. Although the IL application in microwave irradiation technique is still early investigated in order to make it more economically competitive with the conventional heating, the idea on energy efficient and effective process route would prospectively make it becoming potential commercial process in the future.

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