DEVELOPMENT OF IONIC LIQUID AS CATALYST FOR TRANSESTERIFICATION REACTION

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ABSTRACT

Ionic liquid had a various uses and among them is as catalyst in a reaction. This research was carried out to synthesis and developed the choline chloride based ionic liquid to investigate their ability as a catalyst in transesterification reaction. The ionic liquid synthesized was choline chloride.2ZnCl$_2$ and choline.2urea based system. Both of the ionic liquid synthesize were characterized by using Infra-red spectroscopy (FTIR) and Nuclear Magnetic Resonance spectroscopy (^{1}H NMR & ^{13}C NMR). Characterization result confirmed the functional group and the structure of the ionic liquids was as expected. Both ionic liquid were applied as a catalyst for the transesterification reaction and the resulting product was analyzed by GC-FID and GCxGC-MS (ToF). The transesterification reaction of palm olein and buthanol with the presence of choline chloride.2ZnCl$_2$ gives 25.7% yields while with the use of choline chloride.2urea gives 25.0% yields. The results show that the acidity of choline chloride.2ZnCl$_2$ and the basic properties of the choline chloride.2urea were not really suitable to be used as catalyst in the transesterification reaction.

INTRODUCTION

The objective of this research is:

1. To synthesis choline chloride based ionic liquid catalyst which is choline chloride.$ZnCl_2$ and choline chloride.urea.

2. To characterized the ionic liquid catalyst system by using Infra-red spectroscopy (FTIR) and Nuclear Magnetic Resonance spectroscopy (^{1}H NMR & ^{13}C NMR).
3. To test the ability of ionic liquid catalyst in the transesterification reaction of palm olein oil.

REVIEW OF THE LITERATURE

Catalysis

Catalysis is a process to increase the rate of chemical reaction with the presence of a substance called a catalyst. A catalyst is not been consumed or being change in a reaction. A catalyst speed up a reaction by providing a set of elementary steps and lowering the activation energy for the reaction. Catalysts have been used widely in industrial chemistry, and the research in the catalysis field is important especially in the area of applied science.

There are two types of catalysis: heterogeneous catalysis and homogenous catalysis. This is depending on the nature of the rate-increasing substance. There also two types of catalyst usually used which is acid catalyst and base catalyst.

Ionic Liquid (IL)

Ionic liquid is a liquid in room temperature (or below 100ºC) which contains ionic substances and synthesized by heating inorganic salt at high temperature. Most IL is much polarized and poorly coordinated which made them very suitable to be used as a catalyst (DePaoli et al. 2003).

The ionic liquid is synthesized by mixing at least two different solid substances and it can be modified to get certain properties based on the final usage. The uniqueness of this liquid is its ability to produce a stable liquid even it is synthesized from the mix of two different salt as shown in the Diagram 1.1.

Diagram 1. Two solid mixed to form a stabil liquid

There are a lots of simple ion combination could be done to produce an IL so that it's possible to produce an ideal IL with the desired characteristic and functions to meets certain reaction needs. The characteristic can be varies easily with the correct choose of anion and cation, and at right concentration for both substance.
Ionic liquid tend to dissolve polar substances while the organic molecules is not dissolve and did not mixed with the ionic liquid. The common problem faced in the industrial chemistry is the problem on separating their product with the catalyst used. But with IL the reaction product could be separate easily by the liquid extraction.

Choline Chloride

There a various type of ionic liquid that can be synthesizes from the salts. In this research we are focused on the use of choline chloride based ionic liquid. The structure of choline chloride is as on Diagram 1.2 (Royal society of chemistry 2008). Choline chloride or 2-hydroxy-N,N,N-trimetiletaminium chloride ($C_5H_{14}ONCl$) is an organic substance which also known as quaternary ammonium salt. This is the latest alternative used nowadays to synthesis IL with mixing simple organic halide salt and complexes with certain metal chloride or any substance that could form a hydrogen bond. The complication agent is functioned to decrease the interaction between anion and cation and then lowering the freezing point of the mixture.

This choline chloride based IL is easy to synthesis and is not toxic but even biodegradable. The characteristic of this IL can easily modified to meet certain needs and the ionic liquid Lewis acid or base also can be modify by choosing different metal or by combining two type of metal (Abbot 2011).

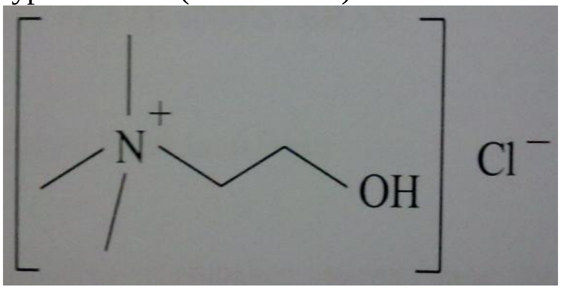

Diagram 2. Structure of choline chloride

Transesterification Reaction

Transesterification reaction is a term normally used to describe an organic reaction where an ester is changed into others form through the alkoxy moiety changing. Transesterification which also known as alcoholysis is the alcohol elimination process from an ester with other alcohol.

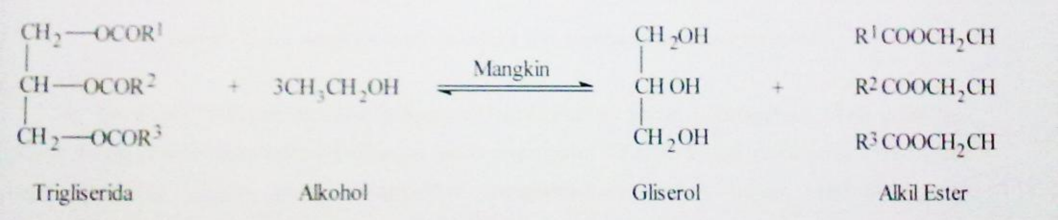

Diagram 1.3 Transesterification reaction

In transesterification reaction, triacylglycerol react with the alcohol with the presence of strong acid or base and produce the mixture of fatty acid alkyl ester and glycerol. Overall process is a series of three reactions which produce di- and mono-glycerides as the intermediate. The reaction stoichiometric requires 1 mole of triacylgriseride and 3 mole of alcohol. However, excess alcohol used to increase the acyl ester product and to form separation phase from the glycerol. Some aspect includes the types of catalyst, alcohol/oil molarity ratio, temperature, the purity of substances (presence of water or moisture) and the free fatty acid content will affect the reaction direction (Schuchardta et al. 1998).

There are two types of catalyst normally used in trnasesterification reaction which is acid and base catalyst. Besides that, biochemical catalyst also had been used which involving the use of enzyme. Transesterification process with the presence of acid catalyst usually resulted in high yields of alkyl ester. However, this reaction is very slow and required high temperature to complete the reaction. While the transesterification with the presence of base catalyst occurred faster than with the acid catalyst. This catalyst is widely used in the industry.

Numbers of research and report have been done to the transeaterification reaction with various catalyst. But yet none of them had reported the use of ionic liquid catalyst in the reaction. Abe et al. (2008) had been reported the research on effect of ionic liquid as catalyst in transesterification reaction but with the presence of biology catalyst. While Lapis et al. (2008) had been used IL just as a supporter in the acid/base catalyzed transesterification reaction.

Fatty Acid Alkyl Ester

Fatty acid alkyl ester is the main product of thransesterification reaction. The product is depends on the fatty acid composition on the oil /fat used. Alkyl ester is a substance which use widely in oleochemical industry. It can be used to synthesis various surfactant and also used in organic synthesis. Alkyl ester can be modified into other chemical substance and was a basic substance for further synthesis.

OBJECTIVE

The objective of this research is:

4. To synthesis choline chloride based ionic liquid catalyst which is choline chloride.$ZnCl_2$ and choline chloride.urea.
5. To characterized the ionic liquid catalyst system by using Infra-red spectroscopy (FTIR) and Nuclear Magnetic Resonance spectroscopy (^{1}H NMR & ^{13}C NMR).
6. To test the ability of ionic liquid catalyst in the transesterification reaction of palm olein oil.

EXPERIMENTATION

Synthesis of Ionic Liquid (IL)

The ionic liquid is prepared by using the established previous method with some modification.

Choline chloride. X zinc chloride ($[ChCl][ZnCl_2]_x$) Ionic Liquid

Ionic liquid from the mixture of quaternary ammonium salt choline chloride and zinc chloride is prepared in the laboratory by adding little by little of zinc chloride into the choline chloride substances which is heated in the oil bath with the temperature increase from the room temperature up to 150°C. The molarity ratio of zinc chloride to choline chloride use is 1:1, 2:1 and 3:1. The melting point of the mixture is observed and record. The mixture is stirred continuously with the glass rod until a homogenous clear liquid is obtained. The resultant liquid will leave on the fume cupboard until a stable ionic liquid obtained. The ionic liquid then analyzed with the Infra-red spectroscopy (FTIR) and the Nuclear Magnetic Resonance spectroscopy (^{1}H NMR & ^{13}C NMR).

Choline chloride. y urea ($[ChCl][urea]_y$) Ionic Liquid

Ionic liquid from the mixture of choline chloride and urea is prepared in the laboratory by adding little by little of urea into the choline chloride substances which is heated in the water bath with the temperature increase from the room temperature up to 80°C. The molarity ratio of urea to choline chloride use is 1:1, 2:1 and 3:1. The melting point of the mixture is observed and record. The mixture is stirred continuously with the glass rod until a homogenous clear liquid is obtained. The resultant liquid must be stable in liquid state even after the reaction. The ionic liquid then analyzed with the Infra-red spectroscopy (FTIR) and the Nuclear Magnetic Resonance spectroscopy (^{1}H NMR).

Characterization of Ionic Liquid

Infra-red spectroscopy (FTIR)

Infra-red spectroscopy is used in this research to study the component and functional group in the $[ChCl][ZnCl_2]_x$ and $[ChCl][urea]_y$) ionic liquid. The ionic liquid obtained is put into vials and send to the Infra-red spectroscopy laboratory.

Nuclear Magnetic Resonance spectroscopy (NMR)

There are two NMR analysis mode use which is proton NMR and carbon-13 NMR. Besides to identify the functional group of the ionic liquid, characterization with NMR also used to verify the $[ChCl][ZnCl_2]_x$ and $[ChCl][urea]_y$) ionic liquid structure. 0.5-0.6ml solvent is added to the 0.03g sample and dissolved until a homogenous liquid obtained and then transferred into the NMR tube for analysis. The solvent used is D-methanol.

Transesterification reaction.

Transesterification reaction is carried out by using 1 mole palm olein oil and 6 mole alcohol (butanol). The oil is stirred with the magnetic stirrer in a three neck conical flask to homogenise the oil. 1% (from the oil weight) of $[ChCl][ZnCl_2]_x$ or $[ChCl][urea]_y$ ionic liquid is then added into the flask then followed by the butanol. The reaction carries on for 3 hours at 100ºC. After 3 hours, the product transferred into a separating funnel. Two phase layers produced, the upper layer is the fatty acid alkyl ester while the lower layer was the glycerol and IL catalyst layer. Usually, the catalyst and glycerol phase is not mixed. Since the quantity of catalyst used is so small that the phase layer cannot be seen clearly.

The lower layer is then separated onto the beaker and the upper layer is washed with warm water three times. Anhydrous sodium sulphate added into the alkyl ester layer to absorb water or moisture that might presence in the product and then its remove by filtration. Next, the alkyl ester layer is evaporated by rotary evaporation to remove excess butanol. The final product obtained is analyzed with gas chromatography (GC) and GCxGC MS ToF. The same method is repeated by using 2% and 5% IL catalyst.

Characterization of alkyl ester from the transesterification reaction.

Gas Chromatography (GC-FID)

Gas chromatography method is use to analyze the fatty acid component in a triacylglycerol (TAG). The analysis performed to identify the fatty acid butyl ester that has been changed during the reaction. 0.1ml of the sample is put into a vial and then added with 1.0ml n-hexane for the analysis.

The parameter used; Model: Hewlett Packred 58900, Solvent: n-hexane, Carrier Gas: Nitrogen Gas, Column: BPX70, Injection temp.: 250ºC, Indicator temp.: 280ºC

Two dimension gas chromatography–Ion time fly mass spectrometer (GCxGC-MS(ToF))

GCxGC-MS(ToF) provide the information of the qualitative and quantitative data of an organic substance with the ability to identify the complex mixed substances. The analysis needed for the product analysed previously with GC-FID that gives the best result based on the peak on the chromatographic. The same sample used for the GC-FID test is used for this analysis.

The GCXGC-MS(ToF) parameter used: Model: GC 6890 N – Agilnt, MS LECO – Pegasus 4D, Solvent: n-Hexane, Primer Column: Rxi-5MS,30M, 0.25mm/D, 0.1um df, Secondary Column: DB-WAX, 1M, 0.10mm/D, 0.1 um df, GC Method: 45(2)-6-230(10), Column Temp.: 250ºC, Injection Volume: 2.0µl, Start time: 35, Finish Time: 450, Electron energy: 70eV, Ion Sources: 200ºC, Time: 42.833 minute.

RESULT AND DISCUSSIONS

Ionic Liquid

The ionic liquid used in this research is based on choline chloride with the complexion agent zinc chloride and urea. The IL is synthesis by mixing the substances while heating. The heating is carries on until certain temperature so that the mixture produced a stable ionic liquid that will not recrystallize and do not vaporize easily even its use later on with high temperature. Diagram 4.1 shows the ionic liquid produced from the reactions.

Diagram 3. Ionic liquid produced

Diagram 4. Fatty Acid Butyl Ester Produced

From the experiment, it's found that the melting point of the mixture is depending on the ratio of the mixture. The best ratio for choline chloride to zinc chloride and choline chloride to urea is 1:2 so that this ratio is used along this research and is taken for further characterization. The choline chloride.$2ZnCl_2$ ionic liquid produced is a Lewis acid IL. This is because of the main anion for Cl was a chlorozincinate anion (Liu et al. 2008). While the choline chloride.2urea IL is alkaline with pH value ~10.

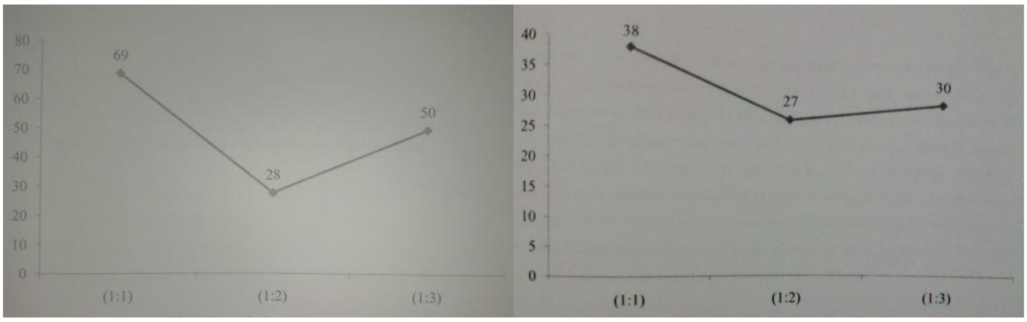

Diagram 5. The melting point changing of choline chloride with zinc chloride and choline chloride with urea at different ratio.

The analysis result as shown below.

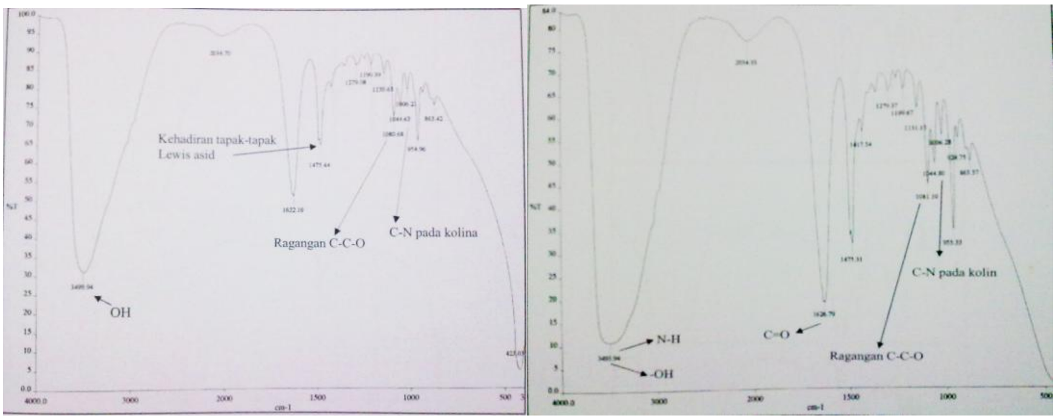

Diagram 6. Infra-red spectroscopy for $[ChCl][ZnCl_2]_2$ and $[ChCl][urea]_2$ ionic liquid

Ionic Liquid as a Catalyst for Transesterification Reaction

The ionic liquid used in the research is an acidic for choline chloride.2ZnCl IL and weak base for choline chloride.2urea IL. Drastic reaction condition required such as high temperature and high alcohol/oil ratio to increase the rate of the reaction. The alcohol used is butanol because the time of reaction needed is shorter than the reaction that carried with the use of methanol (Pryde et al. 1986) besides the use of butanol also needed for the reaction involving high temperature reaction.

The molarity ratio for the reactant use is 1:6, 1 mole of oil is reacted with 6 mole of butanol. High ratio of butanol used to increase the product yields. However, excess butanol also may interrupt the phase separation which also will affect the resultant product.

Table 4.1 The butanolysis reaction yields

Type of catalyst	Butyl ester yields (g)	Glyserol yields (g)	Excess Alcohol (g)
Choline chloride.$2ZnCl_2$	14.22	1.89	9.25
Choline chloride.2urea	13.90	2.01	9.16

0.0226 mol (20g) palm olein oil, 0.1356 mol (10.05g) butanol, 1% (0.29%) ionic liquid, 3hours reaction at 100°C

Table 4.2 The percentage of butyl ester yields from transesterification reaction with different catalyst.

Transesterification reaction	**Type of catalyst**			
	Blank (Without catalyst)	H_2SO_4	Choline Chloride. 2ZnCL	Choline Chloride. 2 urea
Butyl ester yields (%)	0.00	98.80	25.73	25.00

Note: Temp. 100°C, alcohol/oil ratio=30, time=3 hours, catalyst=1%

Fatty acid alkyl ester analysis

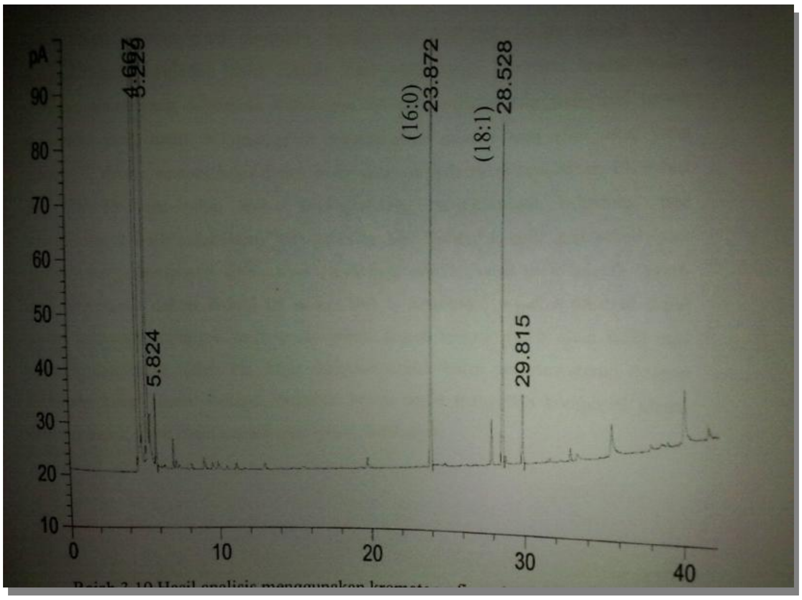

Diagram 7.Gas Chromatgraphy
result

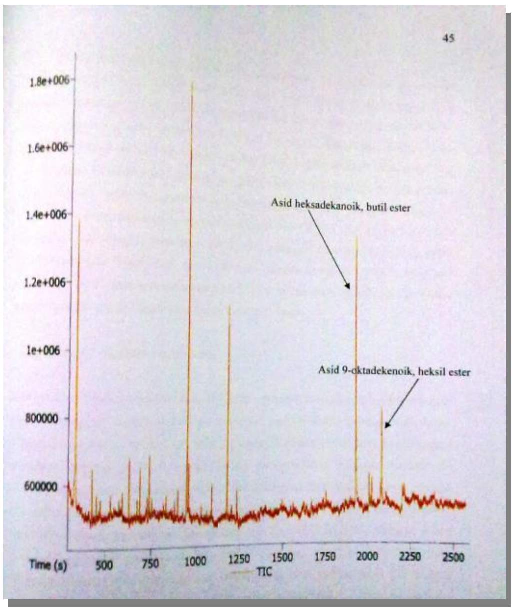

Diagram 8. GCxGC-MIS(ToF) analysis result

Based on the analysis, the conversion of the oil to fatty acid alkyl ester by transesterification reaction with choline chloride based ionic liquid is only yields up to 25.73%. Besides that the conversion of palm olein triacylglycerol (TAG) into fatty acid alkyl ester shows only two type alkyl ester was produced which is butyl palmitate and hexyl oleate. This shows that only the dominant fatty acid is reacted to form alkyl ester. Even with the use of strong acid IL catalyst gives small amount of product may because of the low activity in the active site of the reaction. While for the basic properties IL used here is the weak base which contras with the theory which required strong base for the transesterification reaction. Because of that, the percentage of yields obtained is lower compared to the use of standard catalyst such as sulfuric acid and sodium metokside (>95% yiels).

CONCLUSIONS

In this research the ionic liquid is successfully produced but the function of the choline chloride based ionic liquid as catalyst in the transesterification reaction is not really suitable because the final product fatty acid alkyl ester yields is not that much and not even reach 50%.

REFERENCES

Abbott, A.P., Bell, T.J., Handa, S. & Stoddart, B. 2005. O-Acetelation of cellulose andmanasaccharides using a zinc based ionic liquid. Green Chem 7: 705-707

Alsalme, A., Kozhevnikova, E.F. & Kozhevnikov, I.V. 2008. Heteropoly acids as catalyst for liquid-phase esterification and transesterification. *Applied catalysis A, General* 7 (27): 1-24

DePaoli, D. 2003. Overview: Technical Summaries on Ionic Liquids in Chemical processing.

Dupont, J., Lapis, A.A.M., Oliveira, L.F. % Neto, B.A.D. 2008. Ionic Liquid Supported Acid/base-Catalyzed Production of Biodiesel. *ChemSusChem* 1:759-762

Earle, M.J. & Seddon K.R. 2000. Ionic liquids: Green solvents for the future. Pure Appl. Chem., 72 (7): 1391-1398

Pryde, E.H., Freedman, B. & Butterfield, R.O.*J. Am. Oil Chem. Soc*. 1986, 63, 1375.

Royal Society of Chemistry. 2008. Salty solvents – ionic really. http://www.rsc.org/education/EiC/issues/2005_Jan/salty.asp [7 September 2008]

The Royal Society Summer Science Exhibition. 2003. Ionic liquid: a research project for students. *A Teacher Resources*: 11-12