PREFACE

1. The reasons for the choice of the topic

Biodiesel is considered as an interesting green energy resource as it is a renewable, biodegradable and non-toxic material. Biodiesel has been produced from vegetable oil and animal fat resources. It is nowadays a trend of using non-edible oils and waste resources such as jatropha oil, microalgae oil, animal fat, byproduct acids from refinering process of edible oil and waste frying oil. However, these feedstocks often contains high content of free fatty acids, which would remarkably decrease the effect of base catalysts. Therefore, acid catalyzed process is preferred.

In recent years, a new generation of catalysts based on ionic liquids (ILs) has been focused on studying. In biodiesel synthesis, IL-catalysts have both advantages of homogeneous and solid heterogeneous catalysts. Several ILs are catalysts effectively for the esterification and transesterification reaction.

The research of biodiesel production using heterogeneous catalysts has obtained many results in Vietnam. However, the research of biodiesel production using IL-catalysts still hasn’t been studied.

2. Objective and content

The objective of this topic is “Research on synthesis of imidazolium-based ionic liquid catalysts for biodiesel synthesis”.

To reach this objective, the contents of research were planned:

1. Synthesis ILs;
2. Strutural and property characterization of ILs by NMR, IR, TG-TDA, DSC methods;
3. Assessment of catalytic activity of ILs for esterification of oleic acid and transesterification of triolein;

4. Investigation of esterification of fatty acid in present of IL-catalysts;
5. Investigation of transesterification of triglycerides in present of IL-catalysts;
6. Investigation of conversion feedstocks which occur simultaneously esterification and transesterification using IL-catalysts.

3. The scientific and practical meaning

13 acidic IL-catalysts were synthesized. Among of them, 1-decyl-3-methymidazolium hydrogen sulfate $C_{10}mimHSO_4$ and 1-(4-sulfonic acid) butyl-3-methylimidazolium methanesulfonate $mimC_4H_8SO_3H.CH_3SO_3$ are suitable for esterification of fatty acids and transesterification of triglycerid – 2 main reactions in biodiesel production.

4. New contributions

- 13 acidic imidazolium-based ILs were synthesized. The comparison of catalytic activity of 13 ILs in esterification of fatty acids and transesterification of triglycerides was found that $C_{10}mimHSO_4$ suitable for esterification and $mimC_4H_8SO_3H.CH_3SO_3$ suitable for transesterification.
- The dissertation studied esterification of oleic acid using $C_{10}mimHSO_4$ catalyst and transesterification of refined coconut oil using $mimC_4H_8SO_3H.CH_3SO_3$ catalyst. These studies are implemented for the first time.
- The dissertation studied preparation of biodiesel from raw materials containing both free fatty acids and triglycerides (Palm Fatty Acid Distillate-PFAD and jatropha oil) using $C_{10}mimHSO_4$ and $mimC_4H_8SO_3H.CH_3SO_3$ catalysts.
- Biodiesel product had good quality with purity reached 98.86% and meets all the TCVN 7717-07 Biofuel specifications

5. Structure of the dissertation

Dissertation includes 152 pages: the query with 03 pages; General view: 38 pages; Experiment and Methodology: 20 pages; Results and discussion: 67 pages; Conclusions: 03 pages; new contributions of Dissertation: 02 pages; List of published works: 02 pages; Reference manual: 132 reference materials (17pages); Addendum: 35 pages. Dissertation has 25 tables, 64 figures and images.

Chapter 1. OVERVIEW

1.1. INTRODUCTION OF IONIC LIQUIDS

1.2. BIODIESEL

1.3. ACIDIC IONIC LIQUID CATALYSTS

1.4. CURRENT SITUATION OF RESEARCH IN VIETNAM

1.5. RESEARCH ORIENTATION

Chapter 2. EXPERIMENT AND METHODOLOGY

2.1. CATALYST SYNTHESIS

2.1.1. Chemicals

- 1-methylimidazole 99 %, 1-bromobutane 99 % , 1-bromohexane 99 %, 1-bromooctane 99 %, 1-bromodecane 99 %, 1,4-butanesultone 99 %, HBF_4 48 %, CH_3SO_3H 40 %, $NaBF_4$ 98 %, $NaPF_6$ 98 % are from Sigma-Aldrich;
- $NaHSO_4.H_2O$ 98 %, HCl 38 %, H_2SO_4 98 % are from Spectrum China.

2.1.2. Synthesis of ILs with 1-methylimidazolium cation

2.1.3. Synthesis of ILs 1-alkyl-3-methylimidazolium bromide

2.1.4. Synthesis of ILs with 1-butyl-3-methylimidazolium cation

2.1.5. Synthesis of ILs 1-alkyl-3-methylimidazolium hydrogensulfate

2.1.6. Synthesis of ILs with 1-(4-sulfonat)butyl-3-methylimidazolium cation

2.1.7. Determining yield of reactions and purity of IL products

2.2. CHARACTERIZATION METHODS

Analytical techniques for characterizing the structure of catalysts includes: NMR spectroscopy, MS(ESI) spectroscopy and IR spectroscopy.

Analytical techniques for characterizing the thermal properties of catalysts includes: thermogravimetry-differential thermal analysis TG-DTA and differential scanning calorimetry DSC.

Other properties such as acidity, density, viscosity, electrical conductivity were measured.

2.3. CATALYTIC ACTIVITIES OF ILs

2.2.1. Chemicals

- Oleic acid 86 %; triolein 90 %; methanol 99,5 % are from China;
- Refined coconut oil is fromTuong An Company (acid value 0,3 mgKOH/g); PFAD is from Cai Lan Company (acid value 178 mgKOH/g), Jatropha oil is fromVIIC (acid value 34,2 mgKOH/g).

2.2.2. Biodiesel synthesis

Oleic acid (triolein, refined coconut oil, PFAD or jatropha oil) and methanol were added to a three-neck flask having a reflux condenser, and a magnetic stirring apparatus. Carried out heating to reaction temperature. When the temperature stabilized, added the catalyst in. The reactions were carried out at the desired temperature with vigorous stirring. Periodically taken samples and analyzed acid value, viscosity or esters content.

2.2.3. Product purification

After reactions, the reaction mixture was poured into a separating funnel and allowed to settle 2 hours. After that there are two distinct phases observed in the funnel. The upper phase consisted of methyl esters, while IL, excess methanol and water (or/and glycerol) can be found in the lower phase, which was then isolated by decantation. Distilled water (or solution of NaCl 10%) was used to wash the upper phase to remove any impurities present. It was later subjected to remove of water traces and unreacted methanol by putting the sample in the convection oven at 110°C for 8 hours.

2.2.4. Recovering and refining catalysts

Viscous IL could be reused after the methanol, water and glycerol in the lower phase were removed. The excess methanol was removed from the lower phase by atmospheric distillation at 65°C. Water and glycerol were removed by vacuum distillation at 100°C and 200°C. Finally, the ionic liquid was directly reused in subsequent runs.

2.2.5. Analizing products

2.2.5.1. Acid value determination

2.2.5.2. Viscosity

2.2.5.3. Methyl esters content

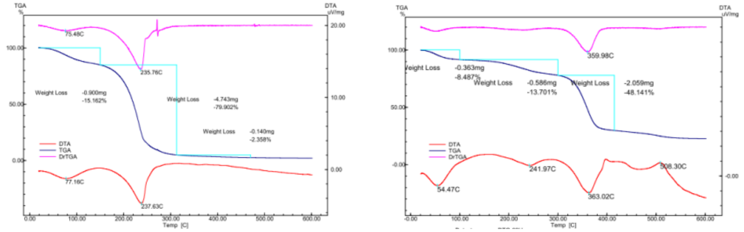
2.2.5.4. Assessment of product quality

Chapter 3. RESULTS AND DISSCUSION

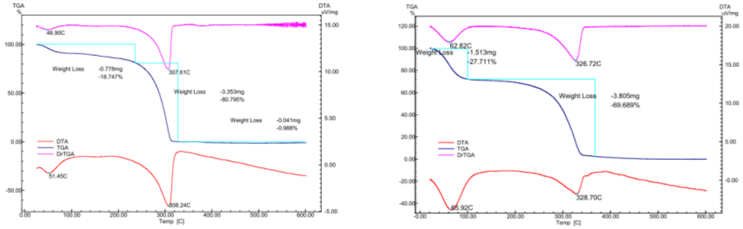
3.1. SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF ILs CATALYSTS

3.1.1. ILs with 1-methylimidazoliumcation

Products analysis results by ^{1}H, ^{13}C NMR and TG-DTA are followed:



HmimCl HmimHSO$_4$



HmimBF$_4$ HmimCH$_3$SO$_3$

Figure 3.2: TG-DTA results for HmimX

- *HmimCl*: ^{1}H NMR (500 MHz, D_2O): δ = 3,889 (s,3H); 7,406 (s,2H); 8,624 (s,1H). ^{13}C NMR (125 MHz, D_2O): δ = 35,517; 119,522; 123,030; 135,029. Decomposition temperature: 235,76°C (fig.3.2).
- *HmimBF$_4$*: ^{1}H NMR (500 MHz, D_2O): δ = 3,906 (s,3H); 7,413 (s,2H); 8,602 (s,1H). ^{13}C NMR (125 MHz, D_2O): δ = 35,607; 119,656; 123,186; 135,194. Decomposition temperature: 307,61°C (fig.3.2).
- *HmimHSO$_4$*: ^{1}H NMR (500 MHz, D_2O): δ =3,791 (s, 3H); 7,308 (s, 2H); 8.525 (s,1H). ^{13}C NMR (125 MHz, D_2O): δ =

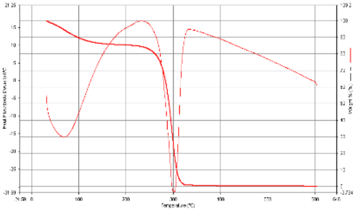
35,582; 119,609; 123,092; 135,131. Decomposition temperature: 359,98°C (fig.3.2).

- *HmimCH$_3$SO$_3$*: ^{1}H NMR (500 MHz, D_2O): δ = 2,759 (s, 3H); 3,893 (s, 3H); 7,410 (s, 2H); 8,623 (s,1H)); ^{13}C NMR (125 MHz, D_2O): δ= 35,628; 38,648; 119,644; 123,161; 135,137. Decomposition temperature: 326,72°C (fig.3.2).

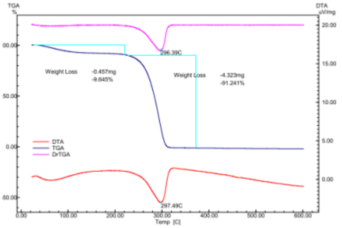
3.1.2. IL 1-alkyl-3-methylimidazolium bromide

Products analysis results by ^{1}H, ^{13}C NMR, IR and TG-DTA are followed:

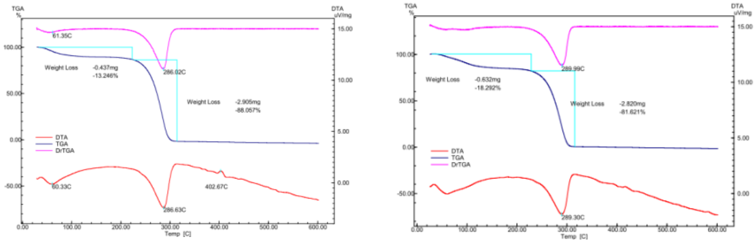
- *C$_4$mimBr*: ^{1}H NMR (250 MHz, D_2O): δ = 0,79-0,85 (t, 3H); 1,21-1,24 (m, 2H); 1,77 (m, 2H); 3,83 (s, 3H); 4,10-4,16 (t, 2H); 7,38-7,44 (m, 2H); 8,69 (s, 1H). ^{13}C NMR (62,9 MHz, D_2O): δ = 12,75 (CH_3); 18,83(CH_2); 31,38 (CH_2); 35,96(N-CH_3); 49,40(NCH_2); 122,21(NCH); 123,61 (NCH); 135,96 (N(H)CN). IR (ν, cm^{-1}): 3143 (=C-H); 3075 (=C-H); 2960 (C-H_3 alkyl); 2872 (C-H_2 alkyl); 1569 (C=N); 1463 (vòng); 1167 (C-C); 753 (C-N); 623 (C-C). Decomposition temperature: 300°C (fig.3.10).
- *C$_6$mimBr:* ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0,86-0,89 (t, 3H); 1,31-1,95 (m, 8H); 4,14- 4,17 (s, 3H); 4,33- 4,36 (t, 2H); 7,38 -7,72 (s, 2H); 10,28 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13,68 (CH_3); 22,11 (CH_2); 25,60 (CH_2); 30,00 (CH_2); 30,80 (CH_2); 36,48 (NCH_3); 49,84 (NCH_2); 121,89 (NCH); 123,61 (NCH); 136,91 (N(H)CN). IR (ν, cm^{-1}): 3143 (=C-H), 3081(=C-H), 2931(C-H_3 (alkyl)), 2859 (C-H_2 (alkyl)), 1571 (C=N), 1466, 1168 (C-C), 761 (C-N), 622 (C-C). Decomposition temperature: 297,5°C (fig.3.10).



C$_4$mimBr



C$_6$mimBr



C_8mimBr C_{10}mimBr

Figure 3.10: TG-DTA results for $C_n$mimBr

- *C_8mimBr:* ^{1}H NMR (500 MHz, $CDCl_3$): δ =0,85- 0,88 (t, 3H); 1,23-1,94 (m, 12H); 4,12-4,14(s, 3H); 4,32-4,35 (t, 2H); 7,55-7,73 (s, 2H) ; 10,25(s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13,99 (CH_3); 22,48 (CH_2); 26,16 (CH_2); 28,86 (CH_2); 28,93 (CH_2); 30,26 (CH_2); 31,58 (CH_2); 36,68 (NCH_3); 50,04 (NCH_2); 122,08 (NCH); 123,84 (NCH); 137,05 (N(H)CN). IR (ν,cm^{-1}): 3144 (=C-H), 3081(=C-H), 2927 (C-H_3 (alkyl)), 2856 (C-H_2 (alkyl)), 1572 (C=N), 1466, 1168 (C-C), 760 (C-N), 623 (C-C). Decomposition temperature: 286,6°C (fig.3.10).
- *C_{10}mimBr*: ^{1}H NMR (500 MHz, $CDCl_3$): δ =0,84-0,89 (t,3H); 1,22-1,92(m,16H); 4,09- 4,14 (s, 3H); 4,29- 4,35 (t, 2H); 7,51(s,1H); 7,69 (s,1H); 10,30 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13,89 (CH_3); 22,43 (CH_2); 26,04(CH_2); 28,78(CH_2); 29,01(CH_2); 29,15(CH_2); 29,23(CH_2); 30,13(CH_2); 31,61(CH_2); 36,54 (NCH_3); 49,93 (NCH_2); 121,86 (NCH); 123,64(NCH); 137,04 (N(H)CN). IR (ν,cm^{-1}): 3145 (=C-H), 3082(=C-H), 2925 (C-H_3(alkyl)), 2856 (C-H_2(alkyl)), 1572 (C=N), 1466, 1169 (C-C), 753(C-N), 622 (C-C). Decomposition temperature: 289,3°C (Fig. 3.10).

3.1.3. IL with 1-butyl-3-methylimidazolium cation

Products analysis results by TG-DTA were shown that C_4mimBF_4 decomposed at 250÷450°C with 2 picks at 270°C and 425°C (fig.3.11); C_4mimPF_6 decomposed at 386,90°C (fig.3.12).

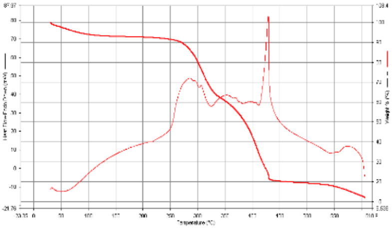


Figure 3.11: TG-DTA results for C_4mimBF_4

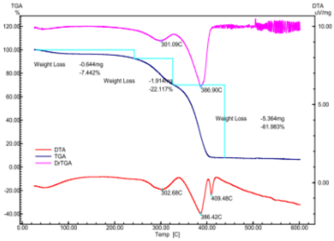
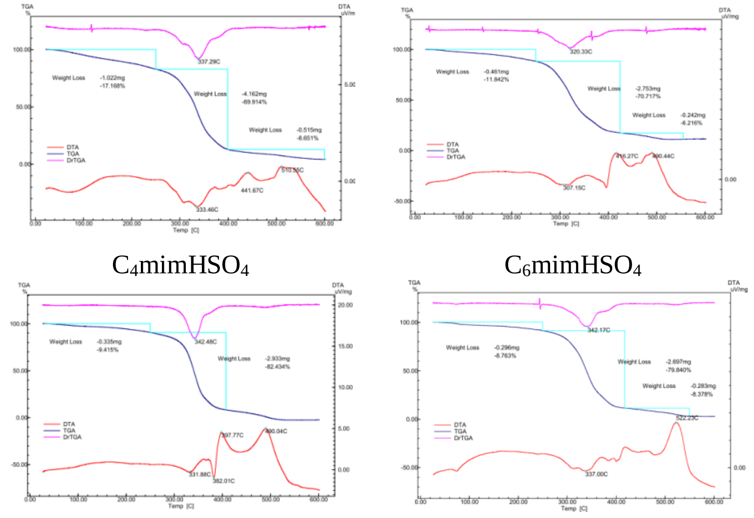


Figure 3.12: TG-DTA results for C_4mimPF_6

3.1.4. ILs 1-alkyl-3-methylimidazolium hydrogensulfate

Products analysis results by ^1H NMR and TG-DTA are followed:

- *$C_4mimHSO_4$*: ^1H NMR (250 MHz, D_2O): δ = 0,91(t, 3H); 1,29-1,32 (m, 2H); 1,85 (m, 2H); 3,89 (s, 3H); 4,20 (t, 2H); 7,45- 7,50 (s, 2H); 8,74 (s, 1H). Decomposition temperature: 337,29°C (fig.3.15).



$C_4mimHSO_4$

$C_6mimHSO_4$

$C_8mimHSO_4$

$C_{10}mimHSO_4$

Figure 3.15: TG-DTA results for $C_nmimHSO_4$ (n = 4, 6, 8, 10)

- *$C_6mimHSO_4$:* ^1H NMR (500 MHz, D_2O): δ = 0,76-0,79 (t, 3H); 1,22 (s, 6H); 1,77-1,80 (t, 2H); 3,81-3,86 (s, 2H); 4,09-

4,13 (t, 3H); 7,35-7,40 (m,2H); 8,62 (s, 1H). Decomposition temperature: 320,33°C (fig.3.15).

- *$C_8mimHSO_4$:* ^{1}H NMR (500 MHz, D_2O): δ = 0,76-0,78 (t, 3H); 1,17-1,22 (m, 10H); 1,77-1,80 (t, 2H); 3,81 (s, 3H); 4,09-4,12 (t, 2H); 7,35 (s, 1H); 7,39 (s, 1H); 8,62 (s, 1H). Decomposition temperature: 342,48°C (fig.3.15).
- *$C_{10}mimHSO_4$:* ^{1}H NMR (500 MHz, D_2O): δ = 0,74-0,76 (t, 3H); 1,16-1,22 (m, 14H); 1,78 (s, 2H); 3,83-3,85 (m, 3H); 4,11-4,14 (t, 2H); 7,39 (s, 2H); 8,69 (s, 1H). Decomposition temperature: 342,17°C (fig.3.15). MS(ESI): +m/z: 223,1 (based); 542,9; 862,1(fig.3.16). MS(ESI): -m/z 194,9; 417,1; 736,7 (based); 1055,8; 1152,9 (fig.3.17).

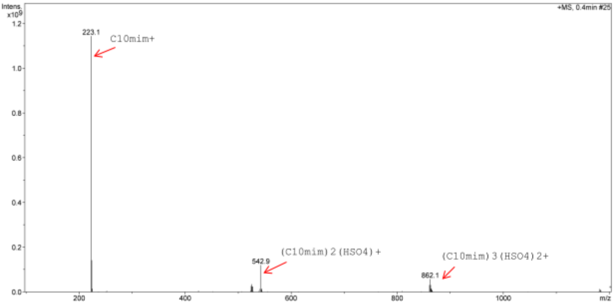


Figure 3.16: MS (+ESI) result for $C_{10}mimHSO_4$

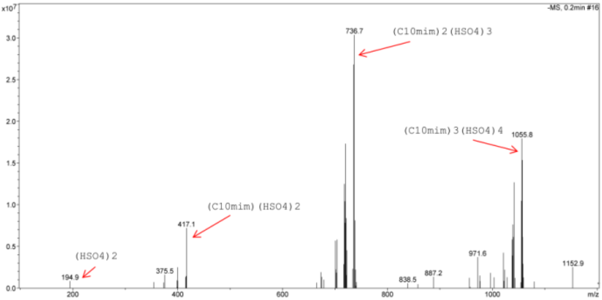
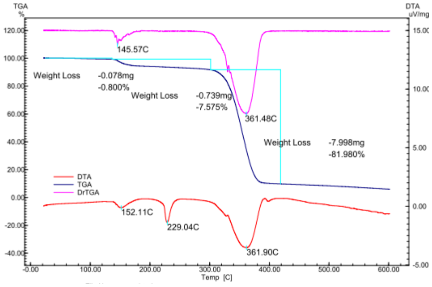


Figure 3.17: MS (-ESI) result for $C_{10}mimHSO_4$

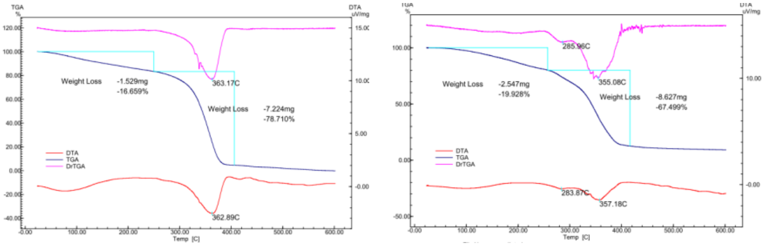
3.1.5. IL with 1-(4-sulfonat)butyl-3-methylimidazolium cation

Analysis results of $mimC_4H_8SO_3H.CH_3SO_3$ and $mimC_4H_8SO_3H.HSO_4$ by ^1H, ^{13}C NMR and TG-DTA are followed:

- *$mimC_4H_8SO_3$:* ^1H NMR(500 MHz, D_2O): δ = 9,242(s,1H); 7,543(m,1H) ; 7,407(m,1H); 4,289 (m,2H); 3,193 (s,3H); 2,868 (m,2H); 2,068(m,2H); 1,822(m,2H). ^{13}C NMR (125MHz, D_2O): 20,919; 28,121; 35,462; 48,792 ; 49,644; 121,915; 122,852; 136,393. Decomposition temperature: 361,48 °C (fig.3.24).
- *$mimC_4H_8SO_3H.CH_3SO_3$:* ^1H NMR (500 MHz, D_2O): 1,772-1,889 (m, 6H); 2,831(m, 8H); 8,078 (m, 2H); 9,194 (s,1H). ^{13}C NMR (125 MHz, D_2O): δ = 21,499; 23,619; 28,586; 36,286; 39,369; 49,313; 122,530; 123,570; 137,056. Decomposition temperature: 363,17°C (fig.3.24).



$mimC_4H_8SO_3$



$mimC_4H_8SO_3H.CH_3SO_3$ $mimC_4H_8SO_3H.HSO_4$

Figure 3.23: TG-DTA results for $mimC_4H_8SO_3$, $mimC_4H_8SO_3H.CH_3SO_3$ and $mimC_4H_8SO_3H.HSO_4$

- *mim$C_4H_8SO_3H.HSO_4$:* ^{1}H NMR (500 MHz, D_2O): δ = 1,618-1,754 (m, 2H); 1,897-2,103 (m, 2H); 2,817-3,215 (t,2H); 3,802 (s,3H); 4,119 (t,2H); 7,316-7,369 (d,2H); 8,597 (s, 1H). ^{13}C NMR (125 MHz, D_2O): δ = 21,051; 28,208; 35,795; 49,036; 50,194; 122,291; 123,792; 136,063. Decomposition temperature: 350,16°C (fig.3.24).

3.2. SCREENING ILs CATALYTIC ACTIVITY

3.2.1. Esterification of oleicacid

The conversions of oleic acid using different ILs are given in Tab.3.11.

Table 3.11: The conversions of oleicacid and pH value of 0.1M IL solutions

N°	Catalyst	Conversion (%)	pH
1	HmimCl	7,62	4,78
2	HmimBF_4	16,50	2,30
3	HmimCH_3SO_3	22,67	1,52
4	HmimHSO_4	19,65	1,61
5	C_4mimBr	7,82	6,58
6	C_4mimBF_4	10,35	5,89
7	C_4mimPF_6	13,71	1,57
8	C_4mimHSO_4	43,59	1,49
9	C_6mimHSO_4	56,20	1,47
10	C_8mimHSO_4	72,35	1,43
11	C_{10}mimHSO_4	78,96	1,28
12	mim$C_4H_8SO_3H.CH_3SO_3$	79,05	1,22
13	mim$C_4H_8SO_3H.HSO_4$	52,43	1,29

**Reaction conditions: 65°C, 2 h, molar ratio ofmethanol/oleic = 2, m(catalyst)/m(oleic)=10 wt.%.*

Thus, out of 13 tested ILs, C_{10}mimHSO_4 and mim$C_4H_8SO_3H.CH_3SO_3$ showed the best catalytic activity. It can be seen, the activity of C_{10}mimHSO_4 slightly lower than mim$C_4H_8SO_3H.CH_3SO_3$ while it costs much lower. So C_{10}mimHSO_4 was selected as catalyst for esterification of fatty acids.

3.2.2. Transesterification of triolein

Results of the methyl esters synthesis using different IL-catalysts are shown in Table 3.12.

Table 3.12: Methyl esters content of products

Nº	Catalysts	FAME (%)
1	HmimCl	1,47
2	$HmimBF_4$	2,73
3	$HmimCH_3SO_3$	1,58
4	$HmimHSO_4$	1,56
5	C_4mimBF_4	2,35
6	C_4mimPF_6	3,69
7	C_4mimBr	1,68
8	$C_4mimHSO_4$	7,50
9	$C_6mimHSO_4$	9,78
10	$C_8mimHSO_4$	11,35
11	$C_{10}mimHSO_4$	15,24
12	$mimC_4H_8SO_3H.HSO_4$	23,16
13	**$mimC_4H_8SO_3H.CH_3SO_3$**	**26,95**

**Reaction conditions: 75°C, 1 h, molar ratio of methanol/triolein/IL = 9/1/0,15*

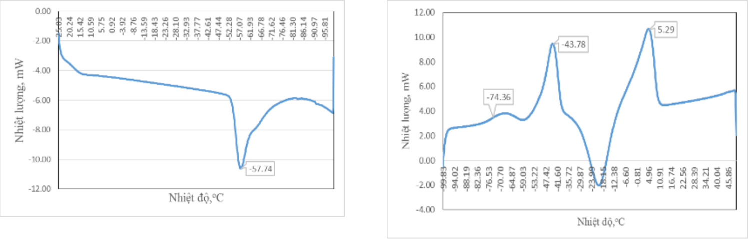
Out of 13 tested ILs, $mimC_4H_8SO_3H.CH_3SO_3$ showed the best catalytic activity. So it is selected for transesterification of triglycerides.

3.3. PROPERTIES OF CATALYSTS

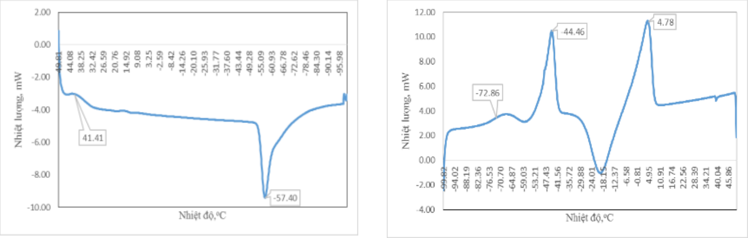
3.3.1. Thermal properties

3.3.1.1. Ionic liquid $C_{10}mimHSO_4$

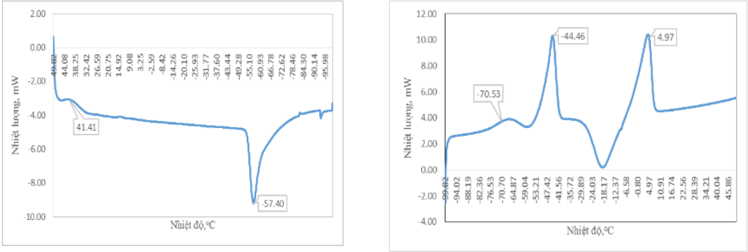
in situ DSC results for $C_{10}mimHSO_4$ (measuring temperature range -100→50°C) were shown in fig 3.26. The results shown that $C_{10}mimHSO_4$ had 5 state transitions in temperature range -100÷50°C. They were melting, crystallization, solid-solid, freezingand glass transition.



Step 1: Cooling   Step 2: Heating



Step 3: Cooling   Step 4: Heating



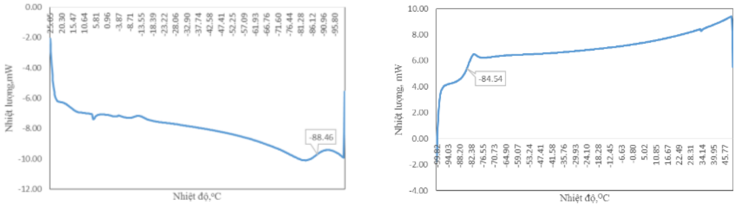
Step 5: Cooling   Step 4: Heating

Figure 3.26: *in situ* DSC results for $C_{10}mimHSO_4$
(Temperature range: -100÷50°C)

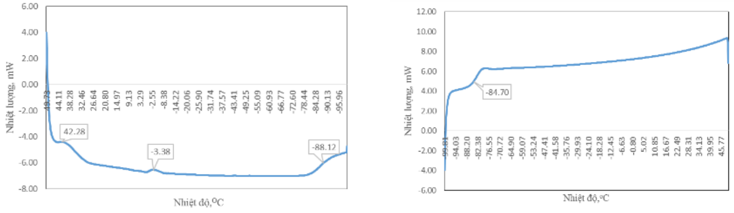
By taking the average value of the measurements, we have melting, crystallization, solid-solid, freezing and glass transition temperature are 5.01°C, -18.6°C, 44.23°C, -57.51°C and -72.58°C, respectively.

3.3.1.2. Ionic liquid $mimC_4H_8SO_3H.CH_3SO_3$

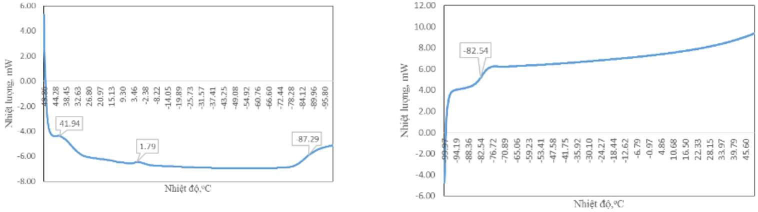
in situ DSC results for $mimC_4H_8SO_3H.CH_3SO_3$ (measuring temperature range -100÷50°C) were shown in fig. 3.29.



Step 1: Cooling   Step 2: Heating



Step 3: Cooling   Step 4: Heating



Step 5: Cooling   Step 6: Heating

Figure 3.27: DSC results for $mimC_4H_8SO_3H.CH_3SO_3$ (temperature range: -100÷50°C)

In fig. 3.27 just observed one state transitions at temperature -85.94°C, characterized the glass transition of $mimC_4H_8SO_3H.CH_3SO_3$.

3.3.2. Density

Density of $C_{10}mimHSO_4$ and $mimC_4H_8SO_3H.CH_3SO_3$ measured by TCVN 3731-82 and was 1.101 g/cm^3 and 1.29 g/cm^3, respectively.

3.3.3. Viscosity

Kinematic viscosities of $C_{10}mimHSO_4$ and $mimC_4H_8SO_3H.CH_3SO_3$ were measured at 100°C and 50°C, respectively. After that, the kinematic viscosity values of ILs will be transfered to dynamic viscosity values.

The results shown that the kinematic viscosity of $C_{10}mimHSO_4$ was 37.5cSt, equivalent to 412.5 cP; the kinematic viscosity of $C_{10}mimHSO_4$ was 24.7 cSt, equivalent to 319 cP.

3.3.4. Electrical conductivity

The results shown that $C_{10}mimHSO_4$ 0.01 M and $mimC_4H_8SO_3H.CH_3SO_3$ 0.01 M solutions have electrical conductivity 0.145 mS/cm and 0.174 mS/cm, respectively.

3.4. ESTERIFICATION REACTION USING IONIC LIQUID CATALYST

3.4.1. Esterification of oleic acid

The effect of reaction time, temperature, reactant ratio, andamount ofcatalyst on oleicacid conversion were investigated and presented in fig. 3.30-3.33.

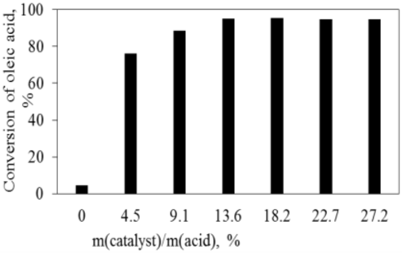


Figure 3.30: Effect of amount of catalyst on oleic acid conversion

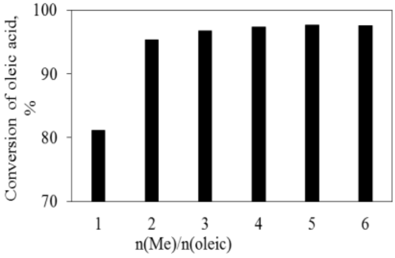


Figure 3.31: Effect of methanol/oleic ratio on oleic acid conversion

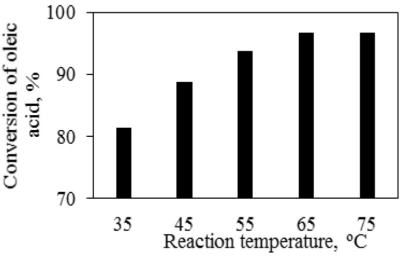


Figure 3.32: Effect of reaction temperature on oleic acid conversion

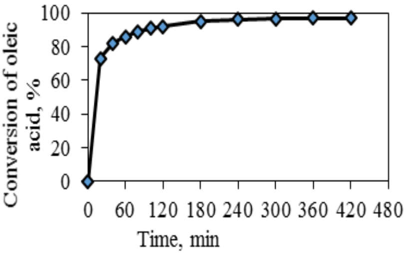


Figure 3.33: Effect of reation time on oleic acid conversion

The above results can be summarised that the suitable conditions for this esterification are 65°C, 4 hours with the methanol/oleic acid=3, 13.6 % catalyst. Under this conditions, oleic acid conversion reached 96.73%.

The kinetic of esterification of oleic acid with methanol catalyzed by $C_{10}mimHSO_4$ was investigated. With molar ratio of methanol/oleic/ionic liquid=3/1/0.12, the reaction was found to be second order with activation energy and pre-exponential factor of 32.17 KJ/mol and 8053.806 min^{-1}, respectively.

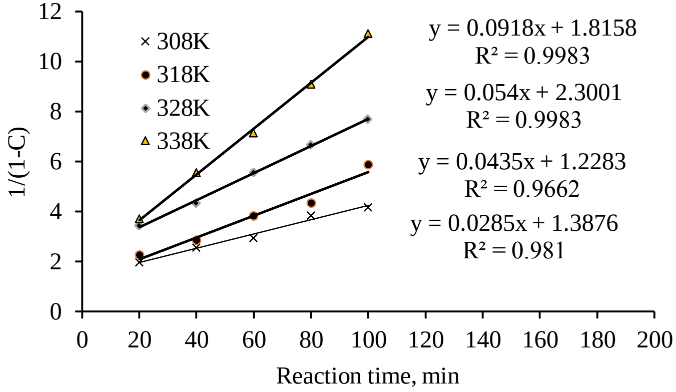


Figure 3.34: Plot of 1/(1-C) versus time

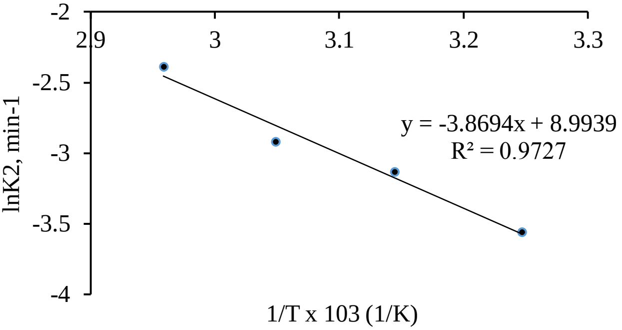


Figure 3.35: Plot of $\ln K_2 = f(1/T)$

3.4.2. Esterification of PFAD

The effect of reaction time, temperature, reactant ratio, and amount of catalyst on PFAD conversion were investigated and presented in fig.3.36-3.39. The survey results show that the suitable conditions for esterification of PFAD with methanol using $C_{10}mimHSO_4$ catalyst are 65°C, 4 hours with the methanol/oleic acid=9, 10 % catalyst. Under this conditions, FAME content of product reached 93.87 %. This value higher than FAME from free fattyacids in PFAD. It means that some FAME was from triglycerides conversion.

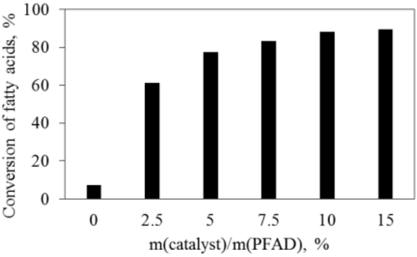


Figure 3.36: Effect of amount of catalyst

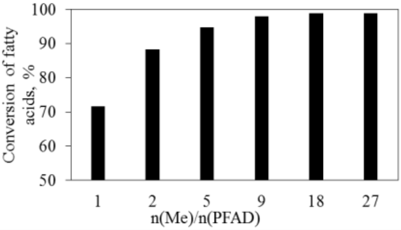


Figure 3.37: Effect of methanol/oleic ratio on oleicacid conversion

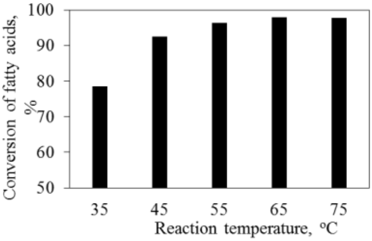


Figure 3.38: Effect of reaction temperature

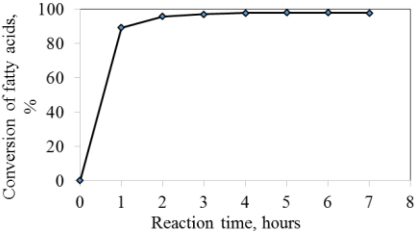


Figure 3.39: Effect of reation time

Thus, $C_{10}mimHSO_4$ can catalyze effectively not only for esterification but also for transesterification.

$C_{10}mimHSO_4$ catalyst could be reused five times at 65°C and the FAME contents of products were not less than 90 %. This indicates that the IL catalyst was recyclable and thermally stable for the esterification.

3.5. TRANSESTERIFICATION REACTION USING IONIC LIQUID CATALYST

3.5.1. Transesterification of refined coconut oil

The effect of reaction time, temperature, reactant ratio, and amount of catalyst on reaction were investigated and shown in Fig. 3.42-3.45.

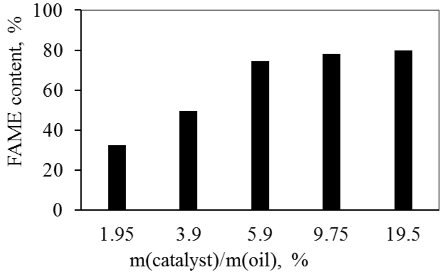


Figure 3.42: Effect of amount of catalyst

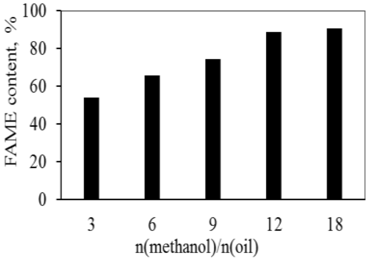


Figure 3.43: Effect of ratio methanol/oil

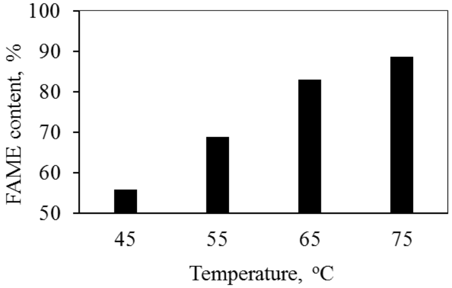


Figure 3.44: Effect of reaction temperature

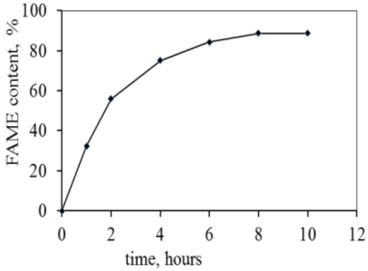


Figure 3.45: Effect of reaction time

The above results show that the suitable conditions of transesterification of refined coconut oil in present of $mimC_4H_8SO_3H.CH_3SO_3$ catalyst are 75°C, 8 hours, amount of catalyst 9.75 % with molar ratio of methanol/oil=12. At those conditions, FAME content of product over 88 %.

3.5.2. Transesterification of jatropha oil

The influence of reaction time, temperature, reactant ratio and amount of catalyst on reaction has been studied and described in Fig. 3.46-3.49.

From the experimental results obtained, we can be concluded that the suitable conditions of transesterification of jatropha oil are 75°C, 8 hours, amount of catalyst 10 % with molar ratio of methanol/oil=10. At those conditions, FAME content of product was 87.76 %.

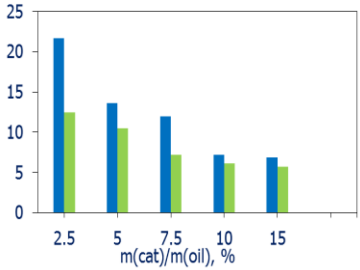


Figure 3.46: Influence of amount of catalyst

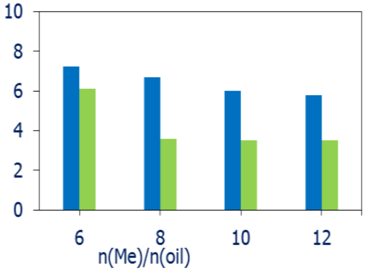


Figure 3.47: Influence of molar ratio methanol/oil

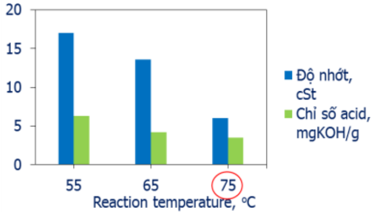


Figure 3.48: Influence of temperature

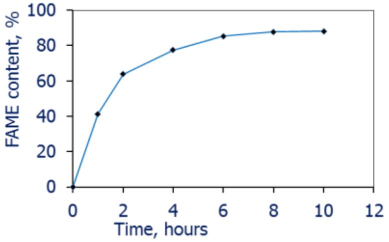


Figure 3.49: Influence of reaction time

$mimC_4H_8SO_3H.CH_3SO_3$ catalyst could be reused six times at 75°C and the FAME contents of products were not less than 83%. This indicates that the IL catalyst was recyclable and thermally stable for the transesterification.

3.6. METHYL ESTE PRODUCTION FROM PFAD

Through 2 reaction rounds at temperature 65°C in 4 hours, acid value was reduced from 178 to 1÷1,5 mgKOH/g.

Table 3.22: Quality of biodiesel from PFAD

Properties	FAME before vacuum distillation	FAME after vacuum distillation
Acidvalue,mgKOH/g	1.1	0.32
FAME content, %	93.87	98.72

The FAME content of product was found 93.87 % by analyzing GC-MS results. After vacuum distillation at 200°C, 0.027 Bar, the product has good quality with FAME content and acid value were 98.72 % and 0.32 mgKOH/g, respectively.

3.7. COMPREHENSIVE ASSESSMENT OF PRODUCT BY TCVN 7717-07

For the comprehensive assessment, the biodiesel product from PFAD was characterized in accordance with the TCVN 7717-07.

Table 3.24: Properties of biodieselderivedfrom PFAD by TCVN 7717-07

Properties	Results	TCVN 7717 - 07
1. Ester content, % mass	98.86	min 96.5
2. Sulfur content, mg/kg	175	max 500
3. Distillation, T90 AET, °C	317.9	max 360
4. Flash Point (Closed cup), °C	213.5	min 130.0
5. Kinematic Viscosity at 40 °C, mm^2/s	4.5	1.9– 6.0
6. Ramsbottom Carbon Residue % mass	0.0158	max 0.050
7. Copper Strip Corrosion at 50°C	1a	N°1
8.Density15°C, kg/m^3	874.2	860 - 900
9.Oxidation Stability, 110 °C, h	6.1	min 6
10. Water & Sediment, % vol	< 0.05	max 0.050
11. Acid number, mg KOH/g	0.50	max 0.50
12. Apperance	pale yellow, clearning, no suspendedimpurities	No water, sediment and suspendedimpurities
13. Cetan number	62.0	min 47
14. Cloud Point, °C	16	Báo cáo^D
15. Sulfated Ash, % mass	0.002	max 0.020

16. Phosphorus Content, % mass	0.0004	max 0.001
17. Iodine number, g iot/100g	56	max 120
18. Sodium/Potassium combined, mg/kg	3.9	max 5.0
19. Free Glycerin, % mass	0.00	max 0.020
20. Total Glycerin, % mass	0.00	max 0.240

The results indicate that the product matches all the TCVN 7717-07 biofuel specifications. Especially, the product has a high methyl esters content, low sulfur content, low carbon residue and none detected glycerol.

CONCLUSIONS

1. We have synthesized and characterized 13 ILs acid Bronsted based on imidazolium. All of them have high purity and high thermal stability.
2. Based on the results of screening catalytic activity, we have chosen the suitable catalysts for esterification of fatty acids and transesterification of triglycerids. In detail, $C_{10}mimHSO_4$ is suitable for esterification because of strong acidity and compatibility with feedstock. $mimC_4H_8SO_3H.CH_3SO_3$ is not only suitable for esterification because of strong acidity but also for transesterification because it is supplemented by active center (SO_3H) in cation.
3. We studied systematically and determined the suitable condition for esterification of oleic acid and transesterification of refined coconut oil (containing only fatty acids or triglycerides) using $C_{10}mimHSO_4$ and $mimC_4H_8SO_3H.CH_3SO_3$ catalysts. We concluded that the $C_{10}mimHSO_4$ and $mimC_4H_8SO_3H.CH_3SO_3$ have high catalytic activity. In esterification reaction, the conversion of oleic acid was 96.73%. In transesterification reaction, the methyl esters content was above 88 %. The reaction conditions are "soft" (65^{o}C and 75^{o}C, atmospheric pressure). The separation of product and the recovery of catalyst are simply. These are the key advantages of ionic liquid catalytic process.
4. We used $C_{10}mimHSO_4$ and $mimC_4H_8SO_3H.CH_3SO_3$ catalysts for synthesis of biodiesel from raw material containing both free fatty acids and triglycerides (PFAD and jatropha oil). We have confirm the suitable conditions for converting PFAD and jatropha oil:
    - Converting PFAD in present of $C_{10}mimHSO_4$: 65^{o}C, 4 hours, amount of

catalyst: 10 %, molar ratio methanol/PFAD = 9.

- Converting jatropha oil in present of $mimC_4H_8SO_3H.CH_3SO_3$: 75°C, 8 hours, amount of catalyst: 10%, molar ratio methanol/oil = 10.
- $C_{10}mimHSO_4$ and $mimC_4H_8SO_3H.CH_3SO_3$ can catalyze simultaneously esterification and transesterification.

5. The results of testing biodiesel production from PFAD showed: the acid value reduced from 178 mgKOH/g to 1÷1.5 mgKOH/g after 2 reaction rounds. Biodiesel product had good quality with purity reached 98.86%.

PUBLICATIONS

1. Pham Thi Nam Binh, Nguyen Thi Ha, Dang Thi Thuy Hanh, Vu Thi Thu Ha.*Synthesis of several ionic liquids (ILs) based on 1-butyl-3-methylimidazolium ions and investigation of Ils catalytic activity in oleic acid esterification,* Journal of catalysis and Adsorption, vol. 3 (N^{o}3) 2014, pp.34-39

2. Pham Thi Nam Binh, Dang Thi Thuy Hanh, Vu Thi Thu Ha, Nguyen Manh Ha,*The study of Palm Fatty Acid Distillate conversion to methyl este used1-decyl-3-methylimidazolium hydrogen sulfatas catalyst*, Journal of Applied Chemistry, N^{o}2(30)/2015, pp.12-14

3. Pham Thi Nam Binh, Dang Thi Thuy Hanh, Vu Thi Thu Ha, Mai Tuyen, *Catalytic activity of imidazolium-based ionic liquids for esterification of fatty acids,*Journal of Chemistry, Vol. 53, N^{o}1-2015, pp. 62-68.

4. Pham Thi Nam Binh, Dang Thi Thuy Hanh, Vu Thi Thu Ha, Do Thanh Hai, Tran Van Hieu, *Investigation of transesterification in present of ionic liquid catalyst,*Journal of Chemistry, Vol. 53, N^{o}3-2015, pp. 322-327.

5. Pham Thi Nam Binh, Nguyen Thi Ha, Dang Thi Thuy Hanh, Vu Thi Thu Ha, *Synthesis and application of 1-(4-sulfonic acid)butyl-3-methylimidazolium methanesulfonate catalyst for one-step process preparation of FAMEs from jatropha oil*, Journal of catalysis and Adsorption, vol. 4(N^{o}2), pp.167-173, 2015

6. Pham Thi Nam Binh, Mai Tuyen,Dang Thi Thuy Hanh, Vu Thi Thu Ha,*Highly Efficient Esterification of OleicAcidCatalysed by AcidicIonicLiquids*, Catalysisletters, 2015, Reviewing.

7. Dang Thi Thuy Hanh,Pham Thi Nam Binh,Do Thanh Hai, Nguyen Van Chuc. *Patent for utility solution "Systemand process technologies for continuous production of fatty acid methyl esters (FAME) using ionic liquid catalyst",*DecisionN^{o} 58752/QĐ-SHTT, 24 Sep 2015.

8. Pham Thi Nam Binh, Vu Thi Thu Ha, Mai Tuyen. *Esterification kinetics of oleic acid in the presence of ionic liquid as catalyst.* Journal of Chemistry, Reviewing.