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Thermal conversion of glycerol to value-added chemicals: pyridine derivatives by one-pot microwave-assisted synthesis

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Abstract: One-pot syntheses of the value-added heterocyclic compounds 3-methylpyridine and pyridine using a renewable chemical, glycerol, were achieved in acidic medium by thermal conversion reactions. Condensation/cyclization reactions of the thermal degradation products of glycerol were investigated in situ using different ammonia and acidic moiety producing inorganic ammonium salts under pyrolysis or microwave heating conditions. The reaction parameters were studied in detail and satisfying product yields up to 72% were obtained under optimized conditions. Structural identification of all compounds was accomplished by spectroscopic methods.

Key words: Microwave-assisted synthesis, glycerol utilization, pyridine synthesis, value-added chemicals

1. Introduction

In the developing world, energy demand is rapidly increasing. It is known that the most important energy source, petroleum oil reserves, will run out in the near future. This issue has directed scientists to focus their attention on alternative energy sources. One of the most promising renewable energy sources is biodiesel.[1] The biodiesel process involves transesterification of fats and oil with a small alcohol molecule such as methanol. Meanwhile, large amounts of crude glycerol are formed as a by-product from the transesterification of the oils in biodiesel production. It is known that 1 kg of glycerol is formed per 9 kg of biodiesel produced, and so the effective utilization of glycerol is vital to reduce the cost of biodiesel production.[2,3]

Glycerol is an important substance, having several areas of application, and it is well known that it can be converted into different compounds by various reactions (oxidation, reduction, dehydration, hydrogenation, etc.). Glycerol can also be converted into valuable chemicals such as acrolein, acetaldehyde, formaldehyde, etc. by thermal reactions.[4–6] Conversion of glycerol to acrolein is well known in the literature and has been studied in detail since the 19th century.[7,8] Various solid-acid catalysts have been used for the dehydration of glycerol in either the liquid or the gaseous phase.[9–16] Liquid phase reactions are reported in which various homogeneous or heterogeneous acid catalysts have been used, such as sulfonic acid, benzenesulfonic acid, metal phosphates, metal sulfates, alumina, and zeolites, but only around 25% of the glycerol could be converted into acrolein with low selectivity.[17,18] Degradation, polymerization, and tar formation have been the main side reactions of the liquid-phase dehydration of glycerol.

The gas-phase dehydration reaction of glycerol has been carried out under different conditions in the presence of metal oxides and heteropolyacids (HPAs) supported on metal oxides in autoclaves under high

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pressures and at high temperatures. It was reported that in the gas-phase reactions dehydration of glycerol was more successful and resulted in high yields of acrolein. Synthesis of valuable heterocyclic compounds has been successfully performed from degradation and dehydration products of glycerol, such as acetaldehyde and acrolein, in the presence of ammonia gas. Several examples of gas-phase reactions involving a heterogeneous catalyst (silica/alumina or zeolite) can be found in the literature.[19] Among these catalysts, zeolites and their different modified versions have attracted considerable attention in the synthesis of pyridines. Not only zeolites but also their metal supported derivatives have been used for enhancing the catalyst activity so that pyridine and 3-methylpyridine yields reached up to 80%. Metal ions doped zeolites have been studied and a mixture of mainly pyridine and 3-methylpyridine was obtained with a yield of 74%. The condensation reaction of different aldehydes, such as acrolein, formaldehyde, propionaldehyde, acetaldehyde, and crotonaldehyde, or their mixture with an ammonium salt in the liquid phase, has also been investigated in the synthesis of pyridine derivatives and produced 3-methylpyridine more selectively than pyridine, with moderate yields in general.[20−25] Polymerization of glycerol and acrolein has been the most important problem in these reactions and caused lower yields. In addition, the high costs of the catalysts and their harmful effect to health and the environment as well as complicated purification processes are the main disadvantages of these methods.

In this research, one-pot syntheses of monocyclic pyridine derivatives were investigated by the thermal reaction of glycerol in the presence of an ammonium salt under microwave irradiation. The main benefit of this research was a one-pot reaction in a closed system under microwave heating conditions and it was expected to prevent polymerization of both glycerol and in situ formed acrolein in the acidic medium, thus resulting in higher yields of pyridines. An ammonium salt such as ammonium chloride or ammonium bisulfate was expected to behave as a gaseous ammonia source and also an acid catalyst after thermal decomposition at reaction temperatures over 200 °C.

2. Results and discussion

One-pot syntheses of pyridine and derivatives were investigated by the thermal reaction of glycerol with different ammonium salts using different heating strategies (pyrolysis, microwave) in subcritical conditions. Primarily, the reaction conditions were determined depending on the nature and decomposition temperature of ammonium salts. The reason for using an ammonium salt was to provide an acidic environment needed for the thermal conversion of glycerol to acrolein. Additionally, being readily available and affordable compounds, ammonium salts were used as a nucleophilic nitrogen source for their distinctive property of producing ammonia gas under thermal conditions. Therefore, several ammonium salts were chosen in order to understand their utility in the one-pot syntheses of pyridines from glycerol. The ammonium salts employed in this research work are given in Table 1.

Table 1. Ammonium salts employed and their decomposition temperatures.

Ammonium compound	Melting or decomposition temperature (°C)
$(NH_4)_2HPO_4$	155 °C
$NH_4H_2PO_4$	190 °C (d)
$(NH_4)_2SO_4$	235 °C (d)
NH_4Cl	340 °C (mp)
NH_4OAc	114 °C (mp)
$H_2NNH_2.H_2SO_4$	265 °C (d)

Research studies were performed using pyrolysis and microwave heating and the results obtained were evaluated under 2 headings.

2.1. Pyrolysis experiments

In our preliminary studies, 2 different methods were used, namely batch and flow system pyrolysis.[26] Glycerol was reacted as a raw material at high temperatures in these pyrolysis experiments together with an ammonium salt chosen from the above list, to provide acidic medium for the dehydration of glycerol to acrolein as well as an ammonium source. It was expected that the ammonium salt used would decompose and release the ammonia gas at high temperature. In this synthetic procedure, at first, glycerol is expected to convert into acrolein by the effect of acid catalyst formed in situ by decomposition of ammonium salt. Then a condensation reaction between 2 moles of acrolein molecules with ammonia was anticipated to give the desired heteroaromatics after an aromatization step. Dehydration of glycerol to acrolein was considered to be the difficult stage to handle during the reactions, because both acrolein and other volatile aldehydes may rapidly polymerize and produce some by-products in the reaction medium, and so it may cause tar formation and low product yields.[27]

In order to improve the product selectivity and the product yields, the reaction conditions were studied in detail in both batch (method A) and flow pyrolysis (method B) experiments. Numerous experiments were planned and carried out in order to determine the optimal reaction temperature, glycerol concentration, and glycerol/ammonium salt ratio. Better results were obtained using 10% aqueous glycerol solution with silica supported $(NH_4)_2HPO_4$ and H_3PO_4 mixture as reagent/catalyst by heating at 450 °C according to method B, and the target products, pyridine and derivatives, were obtained in approximately 40% yield in total. Other ammonium salts were also used under similar conditions, but lower yields of pyridines were obtained. The chemical structures of the pyridine derivatives were identified by GC-MS analysis of crude products. A mixture was obtained of mainly 3-methylpyridine and pyridine, together with ethylpyridine and ethyl,methylpyridines in smaller quantities. These results demonstrated that during thermal degradation of glycerol both acrolein and acetaldehyde were obtained as major products in various quantities depending on the acid and ammonia concentrations. These degradation products came together in different proportions and reacted with ammonia in the gas phase, resulting in the formation of mainly pyridine and 3-methylpyridine. On the other hand, it was observed that the obtained yields did not exceed 40%, because of uncontrolled formation of acrolein, which also polymerizes competitively instead of reacting with the ammonia in acidic medium at high temperatures. Below some of the optimized results of pyrolysis experiments are given (Table 2).

Table 2. Results of some pyrolysis experiments.

Entry	Method	Catalyst	Heating rate (°C/min)	rate rate rate	Crude product yield* (%)
1.9 g Glycerol + 5 mL 0.005 M H_2SO_4 + 5 mL H_2O	B	$(NH_4)_2HPO_4$ - 2 g	35	75	25%
1 g Glycerol	A	$(NH_4)_2HPO_4$ - 1.6 g	90	15	36%
1 g Glycerol + 3.2 mL H_2O	B	$(NH_4)_2HPO_4$ -1.6 g	90	60	38%
1 g Glycerol + 7.2 mL H_2O	B	$(NH_4)_2HPO_4$ - 1.6 g	90	60	40%
1 g glycerol + 3.2 mL H_2O	B	H_3PO_4 supported 0.5 g silica gel-$(NH_4)_2HPO_4$ - 1.6 g	90	60	30%

*Calculated yields based on 3-methylpyridine

2.2. Microwave-assisted synthesis

The pyrolysis experimental results showed that the pyrolysis conditions were not adequate because of the low yields of target compounds and also the polymerization problem. We applied another approach for the synthesis of pyridine and derivatives. According to this method, one-pot synthesis of pyridines was studied using glycerol and ammonium salt in a closed vessel and the reactions were carried out by microwave heating under pressure without using any solvent or catalyst.[27] This method provided 2 important advantages: shortening of the reaction time and achieving the reaction in a closed vessel, which serves like an autoclave.

Different ammonium salts were employed in these reactions again in order to provide ammonia gas and acidic medium by decomposition under thermal conditions. Nontoxic, economical, and easily available ammonium salts such as $(NH_4)_2HPO_4$, $NH_4H_2PO_4$, $(NH_4)_2SO_4$, NH_4Cl, NH_4OAc, and $H_2NNH_2.H_2SO_4$ were preferred. Although the decomposition temperature of the ammonium salt was taken as a reference low temperature for the experimental studies, a survey of the temperature range was carried out to determine the optimal reaction temperature. Results of repeated temperature optimization experiments demonstrated that conversion of glycerol to acrolein increased above 250 °C, but it was observed to be a disadvantage due to increased polymerization at high temperatures due to uncontrolled acrolein formation and caused lower product yields. The chemical content of the products was identified by GC-MS analysis. Purification of the products was not dealt with at this step; quantitative analyses of pyridine and 3-methylpyridine were monitored using HPLC. 3-Methylpyridine and pyridine were observed to be the main products, together with ethyl,methylpyridine and some pyrazine derivatives obtained as by-products in lower quantities. Some of the better results obtained from the one-pot synthesis of pyridine derivatives are given in Table 3.

Table 3. Summarized results obtained from optimization experiments.

Glycerol (g)	Ammonium reactive (g)	Temperature (°C)	Reaction period (min)	Crude product yield* (g)
0.54	$(NH_4)_2HPO_4$ - 0.81	280	20	68%
0.59	$(NH_4H_2PO_4)$ - 0.88	250	20	4%
0.54	NH_4Cl - 0.81	270	40	66%
0.58	$(NH_4)_2SO_4$ - 0.87	280	20	34%
0.50	$H_2NNH_2.H_2SO_4$ -0.86	200	30	23%

*Calculated yields based on 3-methylpyridine

The results summarized in Table 3 demonstrated that crude product yields are lower than expected due to polymerization, which was observed as tar formation in the reaction vessel. It is well understood that acrolein formation, or in other words glycerol degradation, is the key step of the reaction. Glycerol degradation to acrolein and acetaldehyde was followed by 2 competitive reactions, coupling/condensation/cyclization of acrolein to heteroaromatics and polymerization of acrolein. Therefore, excessive formation of acrolein is supposed to increase the polymerization rate. Therefore, it is assumed that controlling the rate of this step could be crucial to reduce the polymerization. In order to reduce the amount of free glycerol in the reaction medium, as in the Skraup synthesis, which is well known in the literature, acetic acid has been used for converting glycerol into its mono- and/or diacetate esters in situ.[28–32] Thus, formation of acrolein could have been controlled, so that formation of pyridines would be increased, even in mild conditions. Three different acids, acetic acid, benzoic acids, and $p-$toluensulphonic acids, were used in these experiments to suppress polymerization. The effect of various ammonium salts at different temperatures and reaction times in the presence of an acid catalyst was investigated in detail and the better results are summarized in Table 4. These reactions showed that the

presence of an acid reduced the polymerization reaction and provided satisfactory product yields and acetic acid gave the best results.

Table 4. Effect of an organic acid on the synthesis of pyridine derivatives.

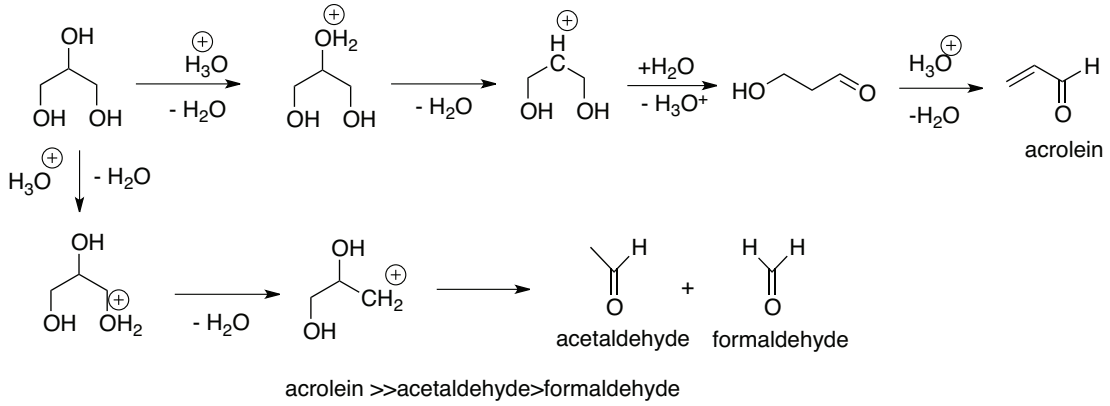
No.	Ammonium reactive (g)	AcOH (mmol)	Temperature (°C)	Reaction period (min)	Yield* (%)
1	$(NH_4H_2PO_4)$ - 0.88	7.3	180	30	52%
2	NH_4Cl - 0.78	5.3	220	20	64%
3	$(NH_4)_2SO_4$ - 0.81	5.5	220	30	35%
4	NH_4OAc - 0.67	8.3	250	30	26%
5	$H_2NNH_2.H_2SO_4$ - 0.42	3.1	200	15	72%
	Ammonium reactive (g)	$p-$TosOH (g)	Temperature (°C)	Reaction period (min)	Yield* (%)
6	$NH_4H_2PO_4$ - 0.62	4.5	180	30	37%
7	NH_4Cl - 0.29	1.2	200	20	14%
8	$(NH_4)_2SO_4$ - 0.81	4.7	220	30	12%
9	NH_4OAc - 0.60	3.5	180	20	6%
10	$H_2NNH_2.H_2SO_4$ - 0.42	2.6	200	20	42%
	Ammonium reactive (g)	PhCOOH (g)	Temperature (°C)	Reaction period (min)	Yield* (%)
11	$(NH_4H_2PO_4)$ - 0.88	4.3	220	20	41%
12	NH_4Cl - 0.78	5.6	250	30	56%
13	$(NH_4)_2SO_4$ - 0.81	5.9	220	30	36%
14	$H_2NNH_2.H_2SO_4$ - 0.42	2.1	200	15	24%

*Calculated yields based on 3-methylpyridine, **5 mmol glycerol was used in each experiment.

It was proved that the formation of acrolein and other volatile aldehydes was slowed down in the presence of an acid, which indirectly controlled the degradation reaction of glycerol, thus reducing the polymerization. Under optimized reaction conditions, the best result was 72% yield of mainly 3-methylpyridine containing a product mixture and it was observed with acetic acid and hydrazine sulfate at 200 °C in 15 min. Analysis of crude products was carried out by characterization with GC-MS and quantitation with HPLC against pyridine and 3-methylpyridine standards and showed that mainly 3-methylpyridine formed together with pyridine. Structural analysis of the 3-methylpyridine and pyridine mixture was also carried out with FTIR and ^{1}H NMR spectra. Integrations values of the protons from the ^{1}H NMR spectrum of the product mixture demonstrated that 3-methylpyridine formed more than pyridine in a ratio of 60:40. These results also proved that under optimal conditions glycerol produces much acrolein by dehydration and degrades to small carbonyl compounds in lower quantities. This result also explains the formation of the main product, 3-methylpyridine, which is formed by coupling and condensation of 2 moles of acrolein. Microwave heating affected the course of the reaction dramatically, shortened the reaction period, and even decreased the reaction temperature. Another advantage of one-pot synthesis was provided by the closed reaction system during microwave heating, where gaseous products were kept inside the reaction medium and forced to react; hence no loss of dehydration and degradation products happened. Five different ammonium salts were employed as a nucleophilic nitrogen source in these experiments within the scope of our work. Although hydrazine sulfate gave the best yield in the presence of acetic acid (Table 4, example 5), other ammonium salts were also found to be useful with different acid reagents (Table 4; experiments 2 and 12).

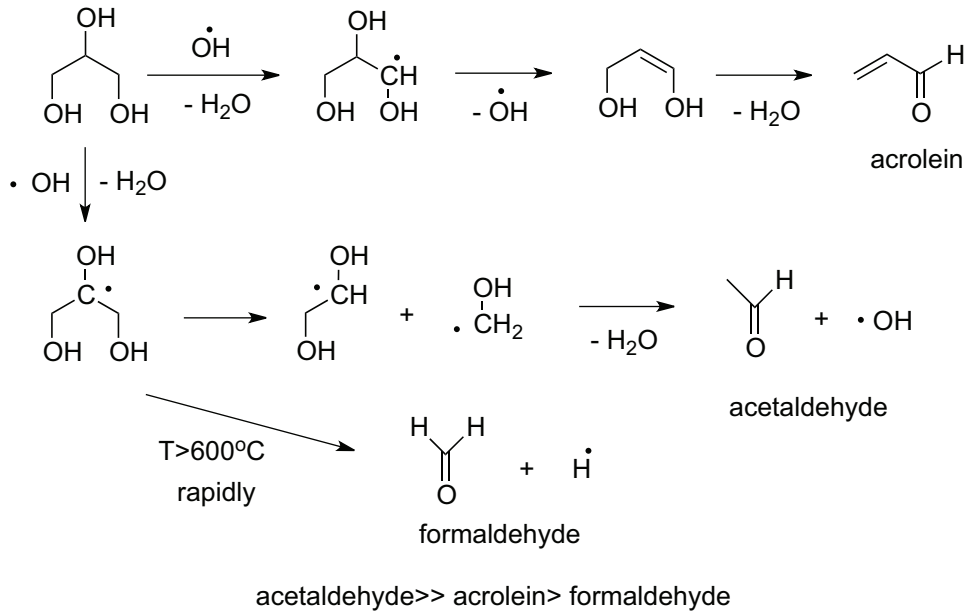
This one-pot synthesis in a closed vessel under pressure of gaseous products by microwave heating was proved to be a better method for the synthesis of heteroaromatics from glycerol instead of open system pyrolysis. A mechanism could be proposed for the one-pot synthesis of 3-methylpyridine and pyridine via formation

of acrolein and acetaldehyde by thermal dehydration and degradation of glycerol in near and supercritical conditions by ionic and radical mechanism, respectively (Schemes 1 and 2).[31] The composition of the product mixture from glycerol dehydration depends on the applied temperature. It means that the proportions of acrolein, formaldehyde, and acetaldehyde in the mixture could be changed with the temperature by competing ionic and free radical reaction pathways.[33] Dehydration of glycerol to acrolein is increased at low temperatures as a result of the ionic mechanism and acrolein is obtained as the main product (Scheme 1).



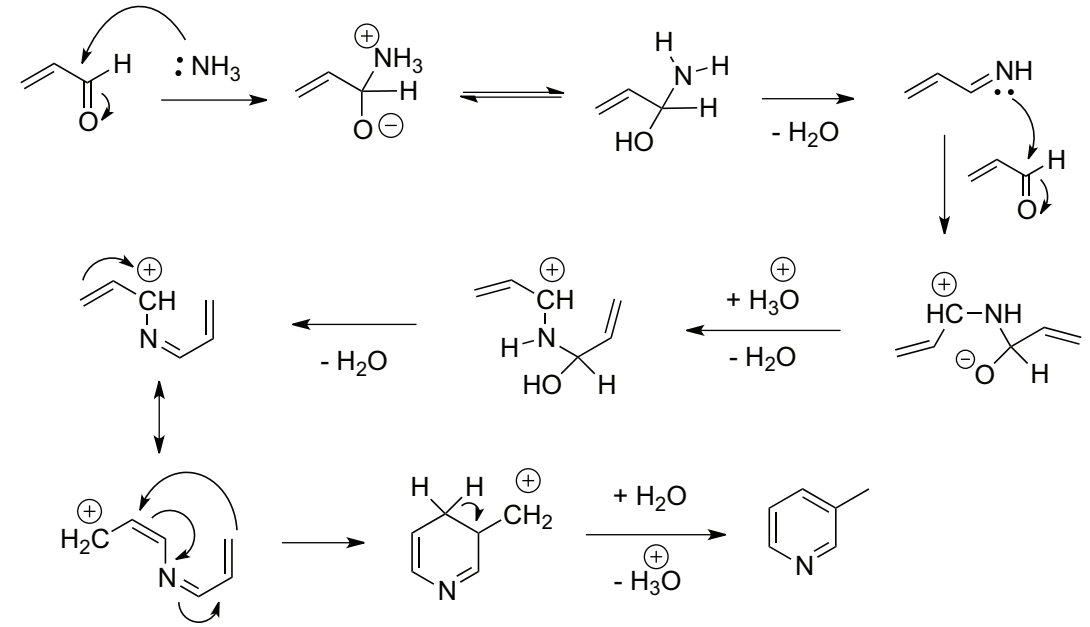
Scheme 1. Synthetic route for the dehydration of glycerol via ionic mechanism.

On the other hand, acetaldehyde occurs mainly at higher temperatures dominantly by a free radical mechanism (Scheme 2).

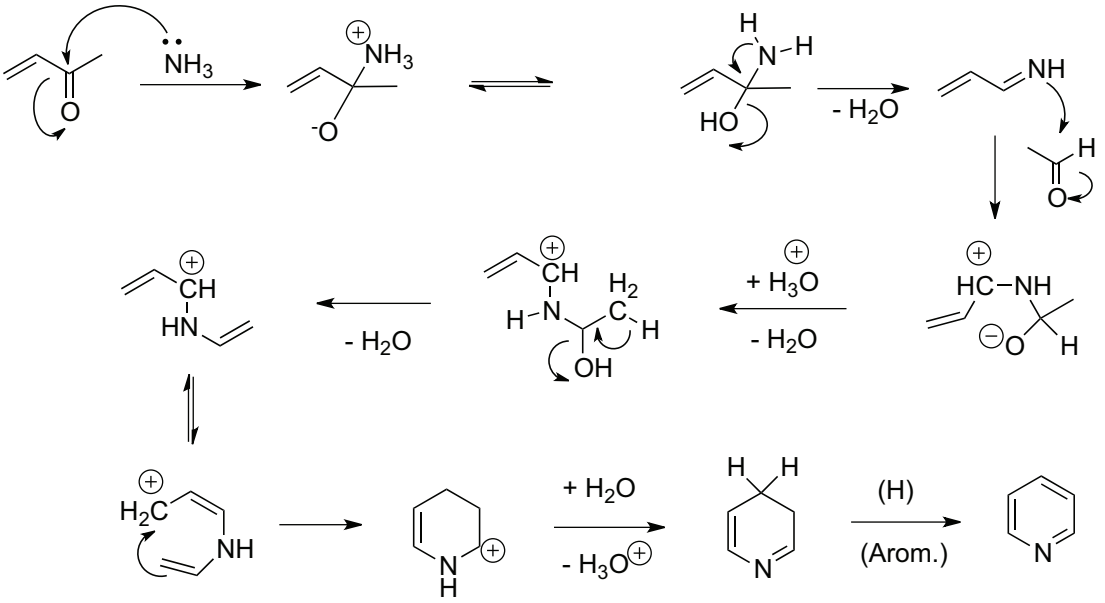


Scheme 2. Synthetic route for the dehydration of glycerol via free radical mechanism.

After the dehydration/degradation step, coupling and condensation of acrolein and acetaldehyde with ammonia result in dihydropyridines, which then aromatize to produce pyridine and 3-methylpyridine. The suggested condensation/cyclization mechanism is given in Schemes 3 and 4.



Scheme 3. Suggested mechanism for the synthesis of 3-methylpyridine.



Scheme 4. Suggested mechanism for the synthesis of pyridine.

The mechanisms described show above that 3-methylpyridine and pyridine might form in separate pathways; while 3-methylpyridine was formed only from acrolein, pyridine formation requires both acrolein and acetaldehyde in equal amounts. Ionic dehydration/degradation produces acrolein as the main product, but together with small amounts of acetaldehyde. In our results, 3-methylpyridine/pyridine ratios were found to be 60:40, which supports the ionic mechanism in the presence of an acid catalyst instead of the radical mechanism.

In conclusion, 3-methylpyridine and pyridine were successfully produced by one-pot synthesis from a renewable chemical, glycerol, by the thermal conversion reaction in the presence of an ammonia producing inorganic reactive under microwave irradiation and pyrolysis conditions. Both products were obtained under

pyrolysis conditions in lower yields (40%) due to undesired polymerization, tar formation, and loss of gaseous products. On the other hand, microwave-assisted heating in a closed vessel resulted in much better yields in much shorter reaction periods. Addition of an acid, such as acetic acid, prevented the polymerization and increased the product yields. Ammonium salts were proved to be highly successful in providing ammonia gas as a nucleophilic nitrogen source and an acid catalyst for ionic dehydration/degradation of glycerol. Direct conversion of glycerol to 3-methylpyridine and pyridine mixture was successfully realized by one-pot synthesis under optimized conditions with yields up to 72%. In conclusion, glycerol, a by-product of biodiesel production, was found to be highly successful as a renewable raw material in the one-pot synthesis of valuable heteroaromatics by microwave-assisted heating in a closed system.

3. Experimental

3.1. Chemicals and instrumentation

All chemicals, including $(NH_4)_2HPO_4$, $NH_4H_2PO_4$, $(NH_4)_2SO_4$, NH_4Cl, NH_4OAc, and $H_2NNH_2.H_2SO_4$, were purchased from Sigma Aldrich or Fluka and used without further purification.

Pyrolytic reactions were carried out using a Protherm pyrolysis furnace and temperature control system. Thermal experiments were carried out in a Quartz tube reactor. A double-walled flask was used for collecting gaseous products in liquefied form, by condensing with a double-walled condenser fitted to the flask. Both collection flask and condenser were cooled by a cryostat at –20 °C set temperature.

A CEM Discovery S-Class (Single Mode) Microwave Synthesis System was used with 35-mL glass vials for the microwave-assisted synthesis reactions. GC-MS analyses were performed using an Agilent Technologies 6890 N Network GC System/Agilent Technologies 5975B VL MSD mass spectrometry. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a Varian-Mercury 400-MHz high performance digital Fourier-transform FT-NMR spectrometer with tetramethyl silane (TMS) as the internal standard. All chemical shifts were given in ppm. IR spectra were recorded on a PerkinElmer Spectrum 100 spectrometer. Quantitative analyses of the products were carried out by Essence HPLC Workstation using an ACE 5 C18 column with 30% aqueous MeOH mobile phase.

3.2. Reactions

3.2.1. Pyrolysis reactions

Two different methods were used for the synthesis of pyridine derivatives, namely batch (method A) and flow pyrolysis (method B).

Batch pyrolysis (method A): 3 g of glycerol and 2.5 g of $(NH_4)H_2PO_4$ were packed into a glass tubular reactor. Nitrogen gas was passed through the system with a flow rate of 40 mL min^{-1} for 20 min before the reaction. The system was heated to a pre-adjusted temperature (450 °C) and the reaction was carried out at that temperature for about 1.5 h. During the reaction, the products were collected in a cooled (–20 °C) reflux condenser fitted flask containing a mixture of H_2SO_4/H_2O (pH 1–2). The products were dissolved in the form of sulfate salt in this solution; therefore after the reaction was completed, this aqueous solution was added to saturated Na_2CO_3 solution to free pyridine derivatives. Pyridine derivatives were then extracted with CH_2Cl_2 (50 mL × 3) and the combined extracts was dried over Na_2SO_4 and evaporated to obtain the crude product.

Flow pyrolysis (method B): Different from the batch pyrolysis, an aqueous solution of glycerol was continuously added dropwise to the sample tub, placed inside the tubular reactor by a thermally stable glass

tube. Thus, $(NH_4)H_2PO_4$ (2.5 g) and H_3PO_4 impregnated silica gel (0.5 g) were prepared in the sample tub and placed into the quartz tubular reactor. Aqueous glycerol solution (20% m/m) was prepared and taken in a dropping funnel. Nitrogen gas was passed through the system with a flow rate of 40 mL min^{-1} for 20 min before the reaction. The Quartz tube reactor was heated to a pre-adjusted temperature (450 °C) and then glycerol solution was added drop by drop and the reaction was carried out for 1.5 h at this temperature, while all the gaseous products were collected in a cooled (–20 °C) reflux condenser fitted flask containing a mixture of H_2SO_4/H_2O (pH 1–2). The products were dissolved in the form of sulfate salt in this solution; therefore after the reaction was completed, this aqueous solution was added to saturated Na_2CO_3 solution to free pyridine derivatives. The pyridine derivatives were then extracted with CH_2Cl_2 (50 mL × 3) and the combined extracts were dried over Na_2SO_4 and evaporated to obtain the crude product.

3.2.2. Microwave-assisted reactions

A mixture of glycerol (1 mmol), an ammonium salt (1.1 mmol), and an acid catalyst was prepared in a 35-mL glass vial and closed with a cap tightly. After stirring, the reaction mixture was irradiated by microwave energy for a few minutes to complete the reaction as required. The reaction mixture was cooled, then treated with water, and then neutralized with aqueous NaOH. The products were extracted with $CHCl_3$ and dried over Na_2SO_4. The extract was evaporated to obtain the crude product, which was purified by column chromatography over silica gel (ethyl acetate:hexane 4:1).

3.3. Spectral data for pyridine and derivatives

The contents of crude products from various reactions were characterized using GC-MS. It was determined that a mixture of 3-methylpyridine and pyridine was obtained together with small amounts of ethylpyridine and ethylmethylpyridine. Quantitative analyses of the 3-methylpyridine and pyridine were carried out with HPLC using a mobile phase consisting of 30% MeOH/70% H_2O. Standard stock solutions were purchased from Sigma-Aldrich and correlation curves for each one were prepared. Calibration curves of the standards ranging from 200 to 2000 ppm were constructed for both eluents. Utilizing the peak area of each component, it was demonstrated that 3-methylpyridine occurred as the main product with a yield of 35%–51%. Chemical structures of the compounds were supported by MS, ^{1}H NMR, and FTIR analysis.

MS of pyridine (EI) m/z (%) calcd. for C_5H_5N m/z: 79 (M^+, C_5H_6N, found: 79 (16)), 52 (100), 26 (10).

MS of 3-methylpyridine (EI) m/z (%) calcd. for C_6H_7N m/z: 93 (M^+, C_6H_7N, found: 93 (15)), 78 (10), 66 (100), 51 (16), 39 (73), 28 (21).

^{1}H NMR spectrum of pyridine ($CDCl_3$), δ_H /ppm: 8.62–8.60 (dd, H, J = 4.8, J = 1.2); 7.68–7.64 (tt, H, J = 7.2, J = 4.8, J = 1.4); 7.28–7.25 (m, H).

^{1}H NMR spectrum of 3-methylpyridine ($CDCl_3$), δ_H/ppm: 8.44 (d, H, J = 1.2); 8.41–8.40 (dd, H, J = 4.8, J = 1.2); 7.48–7.46 (dd, H, J = 7.2, J = 1.4); 7.18–7.15 (dd, H, J = 4.8, J = 2.4); 2.3 (s, 3H).

IR spectrum of 3-methylpyridine ν/cm^{-1}: 3075 (aromatic C–H); 2855 (aliphatic C–H); 1660 (C=N); 1420–1375 (aliphatic C–H); 1594 (aromatic C=C).

IR spectrum of pyridine ν/cm^{-1}: 3046 (aromatic C–H); 1663 (C=N conj.); 1594 (aromatic C=C).

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