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Determination of potential odor causing compounds in the condensate water from the manufacturing process of unsaturated polyester resin

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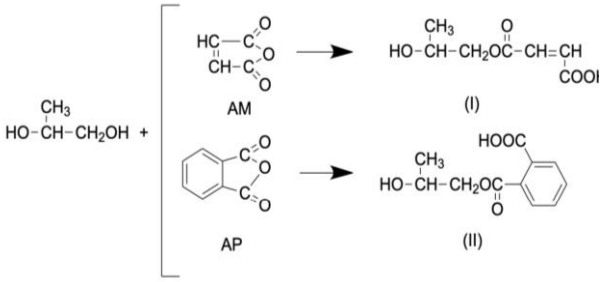
ABSTRACT

Unsaturated polyester resin (UPR) condensate water contains biodegradable organic compounds, including those that create unpleasant odor. Those odors can adversely impact the environment, human health, and, most of all, the uncomfortably. It is important to identify odor-originated chemical compounds to propose a suitable treatment. In this study fractional distillation method to separate volatile organic compounds (VOCs) from UPR condensate water is applied. Fourier-transform infrared spectroscopy (FTIR) and gas chromatography with mass spectroscopy (GC - MS) was used to examine the chemical compounds in URP condensate water. The results showed that unpleasant odors came from the first distillated fraction of URL condensate water, and its composition suggested potential odor compounds of propanoic acid.

Introduction

UPRs are polymer resin that used widely in the fiber reinforced polymer industry because of their low prices, simple operation process, vulcanization process without VOCs, stable dimensionality, and multiple products available [1,2]. UPRs are made from unsaturated and saturated dicarboxylic acid, diol alcohol and an unsaturated compound e.g. styrene. The properties of UPR$_s$ depend on the kind and proportion of the reactants and unsaturated compounds [2]. The most common chemical substances for UPR$_s$ manufacture are 1,2-propylene glycol, phthalic anhydride, and maleic anhydride. The reaction creates UPRs from glycol and acid, or anhydride goes through two steps [3]:

Step 1: Formation of monoester via ring-opening reaction of anhydride with glycol [3].



Step 2: Monoesters from step 1 react with glycol or react themselves to form UPRs and condensate water. This water often consists of 8% raw materials that contains biodegradable compounds [4,5], including VOCs that create an unpleasant odor, whether the

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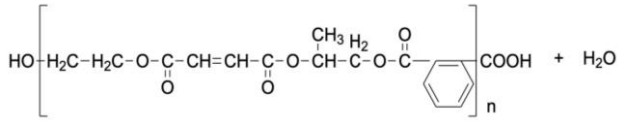
smell is dangerous or not, it is unbearable for human life [6].



The odors from the wastewater negatively impact the community's life, so the effective method has been investigated in many countries recently [6, 7].

It is known that the odors are caused by the presence of volatile organic compounds (VOCs) in condensate water. Often, these compounds are concerned as a health and safety risk. Thus, several methods are used to treat VOCs, such as physical, chemical, and biological methods [8]. To increase the effectiveness of odor treatment, the determination of the compounds is important. Besides, there is almost no study on the chemical composition and well-definite odor-causing VOCs in condensate water from URPs manufacture.

Therefore, in the present study, the FI - RT technique was used to determine the functional groups of raw material, UPRs, UPR condensate water, then VOCs causing odors were separated by the fractional distillation process under vacuum condition. Finally, the GC/MS technique was conducted to detect the chemical substances in the water.

Experimental

Research objects

Condensate water was discharged from the UPRs manufacturing process which used phthalic anhydride (PA); maleic anhydride (MA), and 1,2 propylene glycol (PG) as raw material. This condensate, which is a waste stream, may be hazardous and must be disposed off. The composition and physical properties of condensate water are presented in Table 1.

Table 1: Composition and physical properties of UPR condensate water

No	Parameter	Unit	Value	Vietnamese standard QCVN 40:2011/BTNMT	
				A	B
1	pH	–	5 – 6	6 – 9	5 – 9
2	COD	mg/L	37830	75	150
3	BOD_5	mg/L	16	30	50
4	Odor		unplesant odors	-	-
5	Colour		clear, colorless	-	-

As shown in Table 1, the UPR condensate water contained high concentrations of organic pollutants and which are low biodegradable. According to the Vietnamese standard QCVN 40:2011/BTNMT for industrial wastewater, the chemical oxygen demand (COD) of UPR condensate water is higher than the standard 500 times for A-category and 250 times for B-category Moreover, the COD/BOD5 ratio is 2364, much higher than the criterion for easy biodegradable of >3, so the water is hard to decompose, hardly be biodegrade [11].

The condensate water was separated by the fractional distillation process from 45°C to 50°C to determine composition.

Equipment

Infrared spectra (IR) were determined by Nicolet IS50 FT – IR spectrometer in the mid – infrared region (MRI) with a range (4000 – 400 cm^{-1}) at GeViCat center, Hanoi University of Science and Technology.

The chemical components of URP condensate water were detected by GC Trace 1310 and MS ISQ700 system, using the TG-SQC GC column 15 m x 0.25 mm with the temperature program: 40 °C remain 3 min, increase 10 °C /min to 220 °C in 5 min at GeViCat center, Hanoi University of Science and Technology.

Results and discussion

Determine the functional groups by IR spectra

Functional group adsorbs the IR light at specific wavelength [10]. Therefore, the IR spectra were used to estimate the functional groups of chemicals in products and condensate water.

IR spectra of raw materials and UPRs

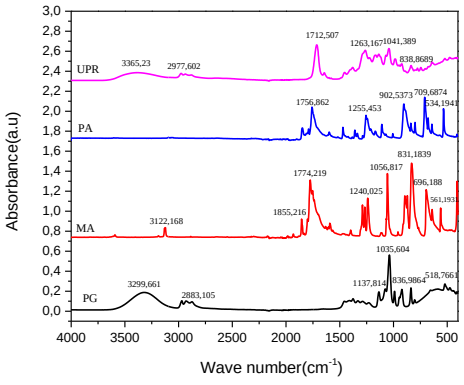


Figure 1: IR spectra of raw materials and UPRs

IR spectra of raw material and UPRs were shown in Fig 1. The peaks in the region of 3000-3500 cm^{-1} in the IR spectra of UPR are the stretching vibration O–H of hydroxyl group compounds (polyalcohol). They are characteristic of the propylene glycol component. The peak at 1770 cm^{-1} reflects vibration C=O in anhydride compounds (1750–1800 cm^{-1}). The results of FT-IR analysis indicated that there is some specific functional groups of propylene glycol, anhydride maleic, and anhydride phthalic in UPRs.

IR spectra of UPR condensate water

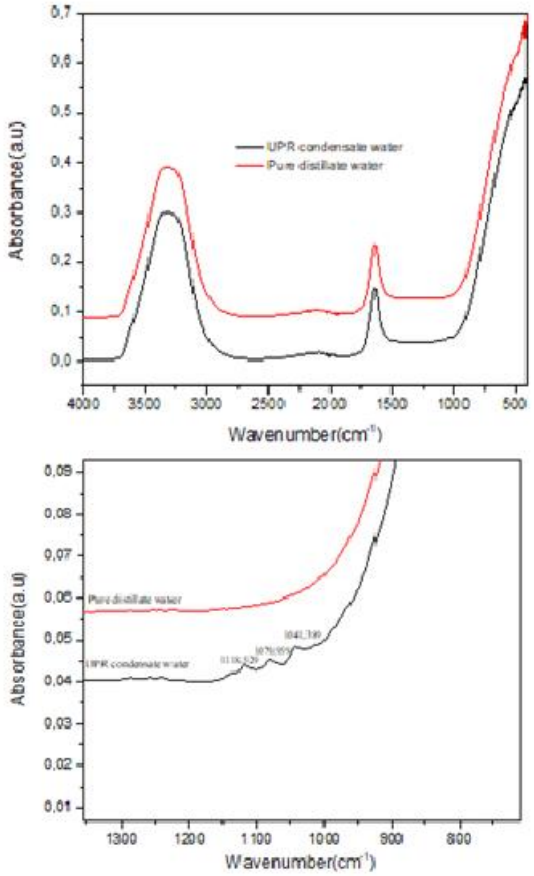


Figure 2: IR spectra of UPR condensate water, pure distillate water and large magnification in the range of 1400-700 cm^{-1}

Fig 2 shows the IR spectra of UPR condensate water and pure distillate water. Two extreme high peaks at 1639 cm^{-1} and at 3309 cm^{-1} corresponding with O–H stretching and O–H–O scissors-bending, belong to water are found [12,13]. The spectrum of UPR condensate water is different from pure distillate water in the presence of intense absorption peak numbers from 1043 to 1120 cm^{-1}, reflecting vibration C=O of the alkoxy group.

IR spectra of UPR condensate water after evaporation at room temperature

To determine the natural volatile ability of organic compounds in the UPR condensate water, a flask containing 100 mL of this solution was put in a fume hood with the opened the lid. After 5 to 10 days, the solution is completely odorless. The IR spectra of the solution, UPR condensate water and pure distillate water were shown in Fig 3

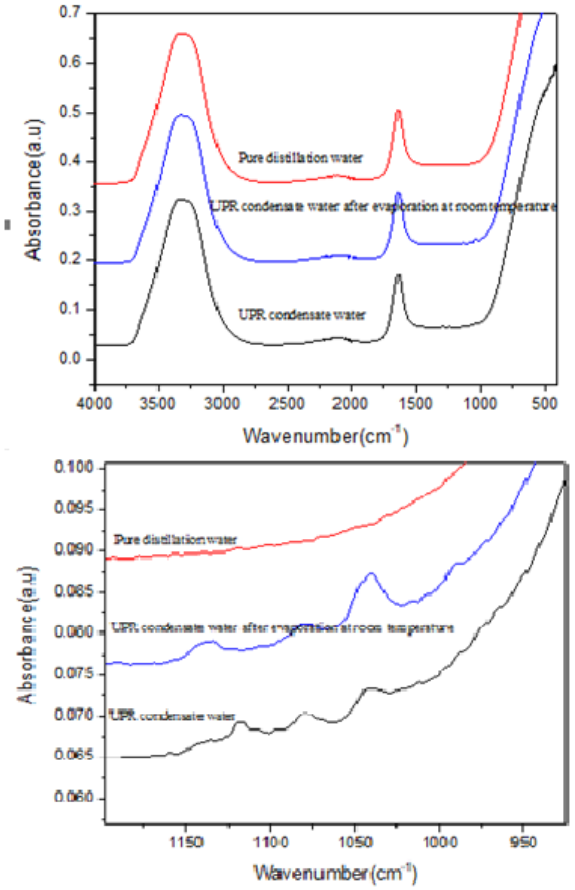


Figure 3: IR spectra of UPR condensate water, UPR condensate water after the natural evaporation for 10 days, pure distillate water and large magnification in the range of 900-1200 cm^{-1}

The IR spectra of UPR condensate water after natural evaporation consists of peaks as similar to that of UPR condensate water with the lower density of the peaks in 1120 - 1040 cm^{-1} range (Fig. 3). The peaks in this range indicated the vibration of C=O bonds (alkoxy), which may be referred to as characteristic of CO-O-CO stretching, C-O stretching in anhydride, alcohol substance [11]. However, UPR condensate water after evaporation has a higher intensity than UPR condensate water because water and VOCs evaporate, increasing the concentration of chemical compounds.

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Pretreatment process

Heating process

Heating process is applied to remove VOCs and determinate the properties of odor-originated chemical compounds. In this study, 500 mL of UPR condensate water was heated to reach 50^{0}C in 30 minutes. The IR spectras of water are shown in Fig 4.

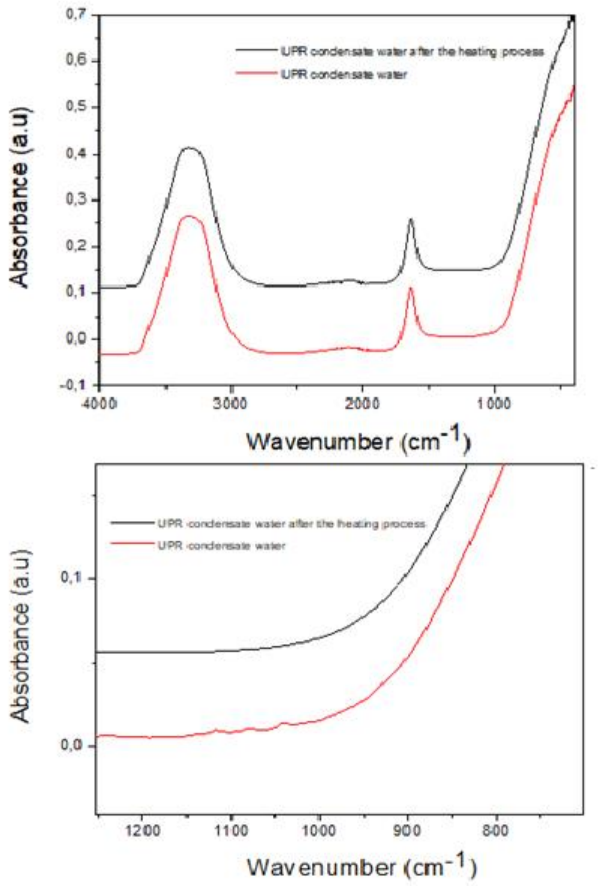

Figure 4: IR spectra of UPR condensate water, UPR condensate water after the heating process and large magnification in the range of 1250-700 cm^{-1}

After the heating process in 30 minutes, the UPR condensate water evaporated, led to a lower water level and slightly decreased UPR condensate water's odor. It is observed in Fig 4 that some intense absorption peak numbers at wave number of 1043 to 1120 cm^{-1} were removed from UPR condensate water after the heating process. Thus, odor-causing chemical compounds can be VOCs so they can be determined by the distillate process, and the evaporating process can happen at about 50^{0}C.

The combined heating with the aeration process

The process heating combination at 50^{o}C with aeration 3.5L/min lasted in 2 hours. The IR spectra of the water is presented in Fig 5.

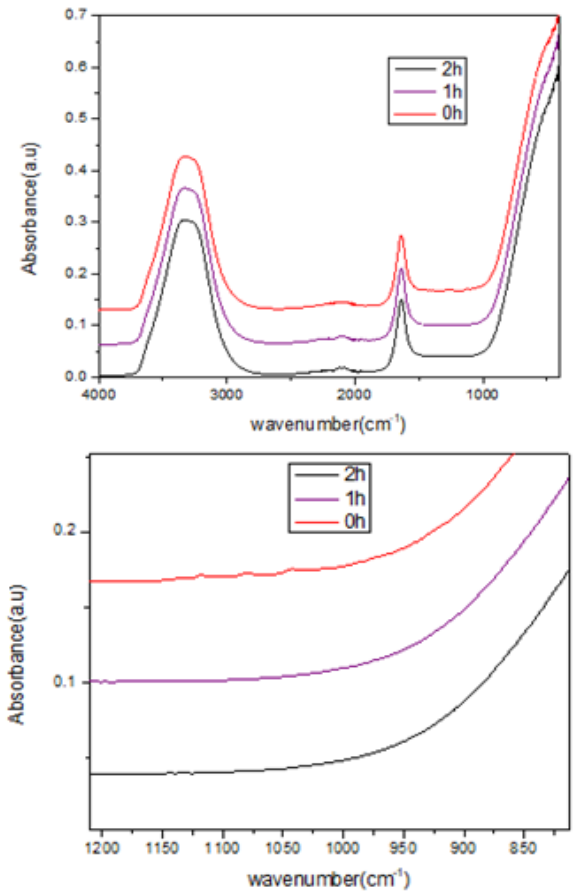

Figure 5: IR spectra of UPR condensate water, UPR condensate water after the combined heating with the aeration process and large magnification in the range of 1200-750 cm-1

IR spectra of UPR condensate water have been changed after the combined heating with the aeration process at one or two hours. Besides sense of the smell of water was decreased. There are no differences in spectra between the heating process and the combined heating with the aeration process (Fig 4 and 5). It was indicated that the chemical compounds in UPR condensate water are mostly slowly biodegradable organic compounds. Thus, the fractional distillation method was used to separate VOCs from UPR water, and then they were identified by the GC-MS technique.

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The catalytic oxidation process

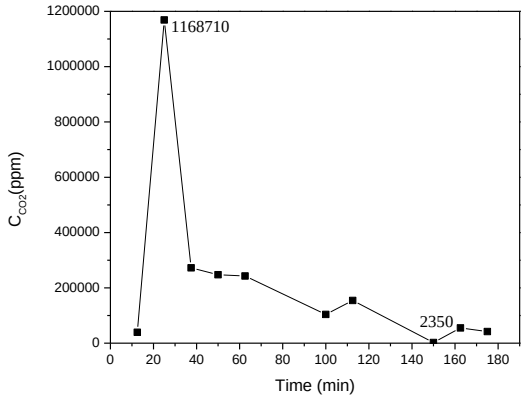

Figure 6: The amount of CO_2 was produced in the oxidation process for treatment UPR condensate water' odor

The MnCoCe/AC catalyst with molar ratio Mn: Co: Ce = 1: 9: 0.19 was used in the oxidation process for UPR condensate water.

The results showed that the amount of CO_2 which was produced in the oxidation process decreased corresponding to the increasing of reaction time. It is also indicated that the organic substances in the UPR condensate water were oxidized by the catalytic oxidation process. However, The performance of this process was still not high, and the condensate water's odor remained for a relative long time due to the low evaporation speed. Therefore, the conditions *(e.g.* pH) for increasing evaporation process of VOCs will be investigated further in next study.

Determine the chemical substances by GC/MS technique

The chemical substance in URP condensate water after evaporation at room temperature

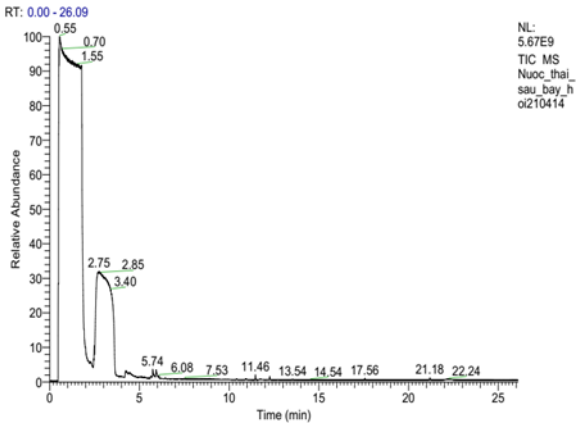

Figure 7: GC/MS profile of URP condensate water after evaporation at room temperature

GC-MS was used to identify the presence of the components in the UPR condensate water. The retention time and mass fragments of chemicals in UPR condensate water were indicated in Table 2**.** The GC-MS profile in Fig 7 has many peaks consists of both URP condensate water and solvent, so the chemical substances in URP condensate water were, respectively, with eight significant peaks as shown in Figure 8.

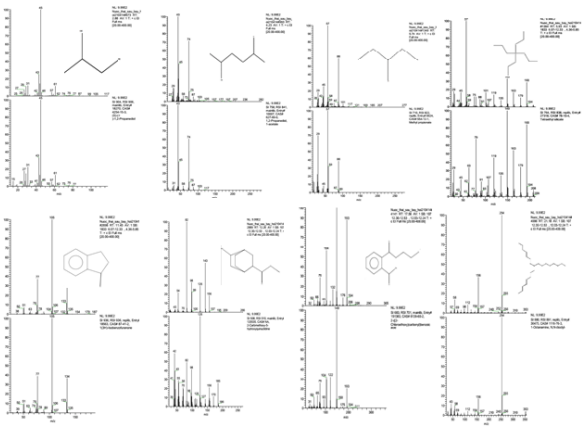

Figure 8: Mass spectrum of chemical subtances after evaporation at room temperature and mass spectrum from the library NIST

Table 2. The chemical substances in UPR condensate water after evaporation at room temperature

No	Substance	RT	MS Fragmentation	Structure
1	1,2 propanediol	2.88	27, 31, 43, 45, 61	
2	1,2 propanediol, 1 – acetate	4.23	43, 45, 58, 74, 75, 87, 103	
3	methyl propionate	5.74	29, 45, 57, 59, 87 and 88	
4	tetraethyl silicate	5.93	29, 45, 91, 107, 119, 135, 149, 163, 179,193	
5	1(3H) isobenzofuranone	11.45	43, 70, 82, 98, 126, 156	
6	2 – carbmethoxy – 5 – hydroxyquinuclidine	12.26	43, 70, 82, 98, 126, 156	
7	2 – (2 – chloroethoxy) carbonyl) benzoic acid	17.56	50, 76, 93, 104, 149, 193	
8	1- octanamine, N, N – dioctyl-	21.18	58, 69, 112, 154, 156, 254, 256	

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Fig 8 shows MS fragement similar to MS fragement of the chemical substances in the NIST library with the certain retention time (RT). The result was presented in table 2.

In summary, 8 chemical substances in UPR condensate water after natural evaporation treatment were shown in Table 2. After evaporation at room temperature, UPR condensate water was odorless.

UPR condensate water after the fractional distillation process

Table 3: COD values of UPR condensate water after the fractional distillation process

No	Sample	Parameter	Unit	Value	QCVN 40:2011/BTNMT	
					A	B
1	The first distillated fraction of UPR condensate water	COD	mg/L	11000	75	150
2	The second distillated fraction of UPR condensate water	COD	mg/L	6900		
3	The third distillated fraction of UPR condensate water	COD	mg/L	52400		
4	The rest distillated fraction of UPR condensate water	COD	mg/L	1400		

To determine the origin of the UPR condensate water's odors, 280 mL UPR condensate water was fractionally distilled in a rotary evaporator under vacuum conditions at three different temperatures, corresponding to 3 steps. Step 1, the water was distilled at 45°C, at speed 120 rpm in 20 minutes, and gained 50 mL of the first distillated fraction of water with pH = 5-6, which had the same odors as origin water. Then, the distillation temperature was increased to 50°C in 20 minutes to obtain 55 mL of the second distillate fraction of water with pH = 4 -5, which had a different odor than origin UPR condensate water. The distillation was kept at the same condition for 20 minutes to obtain 100 mL of the third distillated fraction of wastewater with pH = 5-6, which had a different odor than origin wastewater. The rest layer fractional distillation had a volume of 75 mL with a different smell and pH = 5-6. COD values of the obtained water distillated fraction were shown in Table 3.

Compared with The Vietnamese standard QCVN 40:2011/BTNMT, the chemical oxygen demand (COD) after the fractional distillation process was higher than the standard many times for A-type and B-type. Besides, it was realized that the first distillated fraction of UPR condensate water's odors was the same as the origin of odors in UPR condensate water and had the highest COD value. This distillated fraction step consisted of almost all VOCs. Therefore, the chemical composition of this distillated fraction was identified by the GC – MS. The mass spectrum is shown in Fig 9.

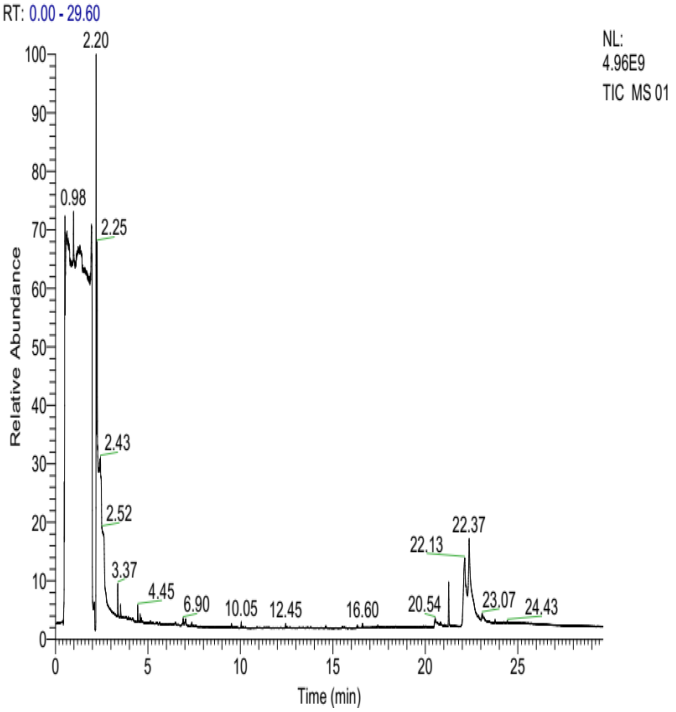

Figure 9: GC/MS profile of the first distillated fraction of wastewater

Fig 10 shows the MS fragments of 29, 45, 73, and 74, similar to MS fragments of propanoic acid with RT=2.20 (unpleasant odor). Fig 10 also indicates the MS fragments of 27, 31, 43, 45, 57, and 61, like the MS fragments of 1,2 propanediol with RT = 2.26 (odorless). Thus, the results showed that odor-originated chemical compound presence in the first distillated fraction of UPR condensate water. The potential odor causing compounds in the condensate water was propanoic acid (CH_3CH_2COOH, bp= 144°C, unpleasant odors).

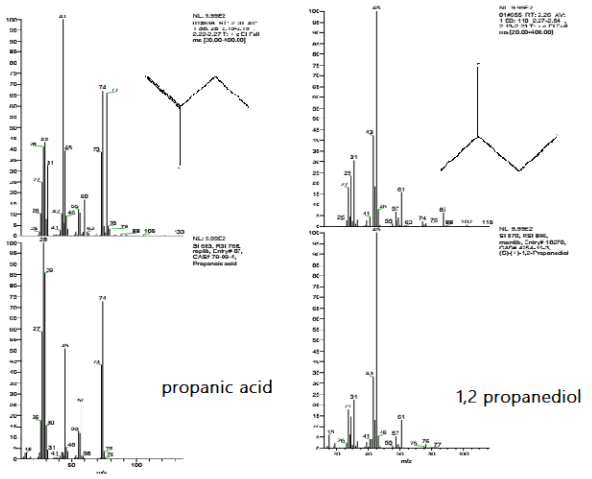

Figure 10: Mass spectrum of other VOCs in the first distillated fraction of UPR condensate water and mass spectrum from the library NIST

Conclusion

In this study, UPR condensate water from URPs manufacture consists of non-biodegradable compounds that create unpleasant odor. Many methods were used to pretreat the odor such as the heating process, the combined heating with the aeration process, the catalytic oxidation. However, odor still remained so the determination origin of chemical subtances is very urgent.

The FT-IR technique was used to determine the functional groups' presence in UPR condensate water. Then, the fractional distillation method separated VOCs of UPR condensate water. Finally, the GC-MS technique was employed to study the component of VOCs that caused unpleasant odors. The results showed that VOCs were in the first distillated fraction of UPR condensate water. The potential VOC was propanoic acid (CH_3CH_2COOH, bp= 144^0C, unpleasant odors).

After the fractional distillation process, COD of all products after the distillated fraction process decrease, but are higher than Vietnamese technique standard QCVN 40:2011/BTNMT. This indicates that the UPR condensate water consists of non biodegradable chemical compounds.

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