

Waste Plastics: Pyrolysis of Powdered and Powder-Free Laboratory Examination Waste Gloves

Authors' contributions

This work was carried out in collaboration between all authors. Author NH designed and set-up the experiment, selected the materials, performed the experiment, operated GC-MS and performed GC-MS analysis, wrote the first draft and finalized the manuscript. Author RM provided GC-MS expertise; participate on the revision of the manuscript. Author SS participated in performing the experiments, and collecting the data, and participated in writing the first draft. Author LL participated in performing the experiments, collecting the data, and performed the statistical analysis of GC-MS data. Author TP participated in performing the experiments, collecting the data, performed the statistical analysis of GC-MS data. Author CO was a part-time participant student during 5 weeks of summer. Author LW had the original idea and supported the work in all steps. All authors read and approved the final manuscript.

ABSTRACT

Aims: The aim of this investigation is to develop a methodology enabling us to clean up the environmental pollution caused by ever increasing amount of plastic materials in the land fields. The procedure however would be practical whenever it is economically advantageous. Thermal cracking of laboratory safety glove (LSG), without catalyst, to useful chemicals is an important part of this program which is reported here.

Study Design: To design the experimental procedure, we primarily concentrated on the thermal stability of the LSG by bearing in mind the results of thermogravimetric analysis (TGA). Based on the thermogravimetric results the appropriate set-up for the decomposition of the LSG was designed.

Place and Duration of Study: The study was done in the Department of Biological and Physical Sciences at South Carolina State University (SCSU), Orangeburg, SC, USA, during the summer of 2013.

Methodology: The thermal cracking process without catalyst was used to convert LSG into liquids and solids useful chemicals. The LSG were push into the reactor one by one without cutting. Prior to pyrolysis, the thermal stability of materials were determined by thermogravimetric analysis (from 50°C to 800°C) with a heating rate of 10°C/min while the samples were purged with 10 mL/min argon. The condensed liquids were analyzed by a Shimadzu GC-MS model GCMS-QP 2010s using helium as the mobile phase.

Results: The thermal stability of the LSG both powdered and powder-free was very similar as was expected since depended on the nature of constituent polymers. The highest decomposition rates were observed at temperatures around 410°C. The (15%) leftover of the powder-free LSG were less than leftover of powered LSG (30%) at 500°C; in the same way the (18%) leftover ashes of powdered LSG was higher than (7%) ashes of powdered free at 800°C. The GC-MS chromatogram of pyrolysis liquids indicated over 350 chemicals. The most abundant compound of pyrolysis was HCl, as was expected from the chemical constituents of chlorinated plasatics, following with eight member carbon isomers, dimers

of dibutene. Also, a variety of phthalic acid derivatives with high concentration were recognized in all samples.

Conclusion: The liquids obtained from pyrolysis of LSGs were a complex mixture of hydrocarbons and cyclic compounds. Also, it was saturated with inorganic and organic acids, esters, and anhydrides. Therefore, the refinement of liquids resulting from pyrolysis is of necessity to obtain a quality fuel. Also, the condensed liquids contained highly reactive chemicals such as acids, alcohols, and alkene, which made them unsuitable fuel for internal combustion engines prior to refinement.

Keywords: *environment; pollution; lab examination gloves; latex gloves, pyrolysis of gloves, neoprene; pyrolysis of waste gloves, chemicals from pyrolysis of gloves*

DEFINITIONS, ACRONYMS, ABBREVIATIONS

Term:

LEG: laboratory examination glove, LSG: laboratory safety glove, PVC: poly(vinyl chloride); PMMA: poly(methyl methacrylate); PS: poly(styrene); PE: poly(ethylene); PET: poly(ethyleneterephthalate); RT: retention time, TIC: total ion chromatogram; GC-MS: gas chromatography-mass spectrometry, WHO: world health organization,

1. INTRODUCTION

Recycling plastics wastes by thermal cracking or pyrolysis is one of the most used methods [1-22]. Pyrolysis has been employed to convert waste plastic into useful products such as fine chemicals, transportation fuels, and lubricant oils. The pyrolysis process uses elevated temperatures to crack down long chain of hydrocarbons and polymers into shorter chain molecules. The waste LSGs in this process decompose randomly into three phases of matter: gaseous materials such as HCl and C1 to C4 hydrocarbons, a complex mixture of liquid, and solid. In this manner, chemical recycling of the stored energies within LSGs waste take place with the environmental advantage of minimizing plastic pollution [1,2].

The safety protection required in scientific laboratories, technological industries, and health industries have an increased demand for the production of latex gloves. As a consequence, the demand for natural rubber latex has raised about four times from 159 k tons in 1984 to 597 k tons in 2003 [1,3]. Since then in 2005, Malaysia, one of the world's leading rubber glove manufacturers, alone consumed 226.2 k tons of natural rubber for glove production [3]. Additionally, the production of natural rubber is expected to increase worldwide. Reports from Indonesia and Malaysia showed effort to increase their output to 2900 k tons and 970 k tons respectively. Also, the private sector in Vietnam is expected to increase their natural demand to 780 k tons, while Cambodia has announced that they expect an increase in their plantation area (45 k tons) [4].

Examination gloves or disposable gloves are used during medical examinations and procedures, and as safety protection in work to prevent contamination.^[5,6] They are available in form of un-powdered, or powdered with cornstarch to lubricate the gloves, making them easier to use [7]. Cornstarch replaced tissue-irritating lycopodium powder and talc. The powders can impede healing if they get into tissues (as during surgery), and can contaminate experiments in laboratory procedures. Therefore, un-powdered gloves are being used more often. Surgical gloves have more precise sizing with a better precision and sensitivity and are made to a higher standard than examination gloves. The gloves that are used in chemistry laboratory as safety protection media are examination gloves (Fig 1a). This type of gloves was the one that were used in the laboratory experimentations, collected during last year; they were pyrolyzed and reported here.

The examination gloves are made of diverse polymers including latex, nitrile rubber, vinyl and neoprene. Neoprene or polychloroprene ($-\text{CH}_2-\text{CCl}=\text{CH}-\text{CH}_2-$)_n is a family of synthetic

rubbers that are produced by free-radical polymerization of 2-chlorobutadiene ($\text{CH}_2=\text{CCl}-\text{CH}=\text{CH}_2$). [8] Neoprene exhibits good chemical stability, and maintains flexibility over a wide temperature range. It is used in a wide variety of applications, such as laptop sleeves, orthopedic braces (wrist, knee, etc.), electrical insulation, liquid and sheet applied elastomeric membranes or flashings, and automotive fan belts. [9]

The decomposition of polymeric materials has been of scientists' interests since the applied knowledge of polymeric materials gained relevance [10,11,12]. The decomposition kinetics of polymeric materials [13,14] and the mechanism of decomposition have been studied by many researchers [15,16]. Researchers have discovered that some widely used polymeric materials such as poly(methyl methacrylate) (PMMA), upon heating, decomposed to original monomers [17] likewise polystyrene (PS) to styrene [18,19,20,21]. However, most of the polymeric materials decomposed to smaller stable molecules that were not original constituents of the polymers. For example, poly(vinyl chloride) (PVC), upon heating, first decomposed to hydrogen chloride and unsaturated polymers which decomposed later to other chemicals [22,23,24]. Pyrolysis of neoprene similar to PVC first produce HCl [25] It is noteworthy that most of the well documented investigations were done on pure polymers with known molar mass distribution or clean materials provided directly by manufacturers. Therefore, the knowledge of decomposition of waste LSGs gained relevance.

The decomposition of polymeric materials is also relevant and of interest to industries since plastic is used in many of today's commodities [26,27]. The pyrolysis of LSGs has attracted the attention of the engineers for designing pilot plants [28]. The wide use of LSGs resulted in the accumulations of untraditional wastes not native to the mother earth life cycle [29]. The disposal of latex gloves in medical wastes, in particular, presents several problems as they are hazardous biologically, non-biodegradable, do generate HCl and chlorinated organic compounds upon incineration, thus the World Health Organization (WHO) is opposed to land filling or incineration of this waste. Therefore, a new technology that is both environmentally friendly and biologically safe would be required to process these wastes. There is still lack of data concerning the characteristics and the kind of product produced for better understanding of the process [28]. A study on kinetic properties of pyrolysis of selected medicals such as absorbent cotton, medical respirator, bamboo sticks [30] and cotton gauge, packaging boxes, capsule plates and transfusion tubes [25] were conducted by a number of researchers.

Actually, wastes of modern materials are accumulated without effective decomposition and recycling routes in the landfills. The increase of petroleum and petrochemical prices opened the ways for industries to invest in recycling of plastic wastes to petrochemicals [31,32,33]. Nowadays, plastic landfills are as valuable as petroleum mines. Models for reaction's kinetics for optimal pyrolysis conditions of plastic waste mixtures have been proposed by researchers. Literature abounds on the recycling of these none-traditional wastes to petrochemicals [34,35,36] and many industries are sustained and developed based on decomposition of natural and synthetic polymers [37,38]. From a scientific-engineering point of view, non-degradability of plastics is no longer an environmental issue in landfills since the plastics can be recycled [39]. However, run-away plastic wastes are continuing to be a huge hazard on the surface and surface water such as waterways, seas and oceans, endangering safe life for both animals and humans [40].

Co-pyrolysis of waste plastic with other natural wastes has been studied. For example, the co-pyrolysis of pine cone with synthetic polymers [41] and characterization of products from the pyrolysis of municipal solid waste [42] and isothermal co-pyrolysis of hazelnut shell and ultra-high molecular weight polyethylene [43] are indicative of the fact that wastes are also useful materials. To avoid the landfill problem and plastic wastes hazards, various techniques for the treatment of waste plastics have been investigated to complement existing landfill and mechanical recycling technologies. The objectives of these

investigations were to convert the waste into valuable products such as fuel, synthetic lubricants, and tar for asphalt pavement before the waste headed to a landfill.

This study reports the results of non-catalytic conversion of examination gloves a neoprene based materials. The material used was waste examination gloves, not freshly prepared polymers, nor clean products supplied by manufacturers.

2. MATERIALS, INSTRUMENTATION, AND METHODS

2.1 Materials

The material used (Figure 1a) was a mixture of un-powdered and powdered waste latex examination gloves (LEGs); which were collected during 2012-2013 in our lab. LEGs were pushed, one by one, into a 5 L three-necked round bottom flask for pyrolysis process.

2.2 Instrumentation

2.2.1 The Thermogravimetric Analyzer

A Perkin-Elmer thermogravimetric analyzer (TGA-7) was used to study the thermal stability of the LEG from 50°C to 800°C with a heating rate of 10°C/min while the sample was purged with 10 mL/min argon. The TGA was calibrated properly before use.

2.2.2 Gas Chromatographer-Mass Spectrometer (GC-MS)

A Shimadzu GC-MS model GCMS-QP 2010s was used to analyze the liquid samples using helium as the mobile phase. The oven program was set on 6 min at 40°C, followed by a 10°C/min temperature increase to 220°C and then an isothermal on the final temperature for 15 min.

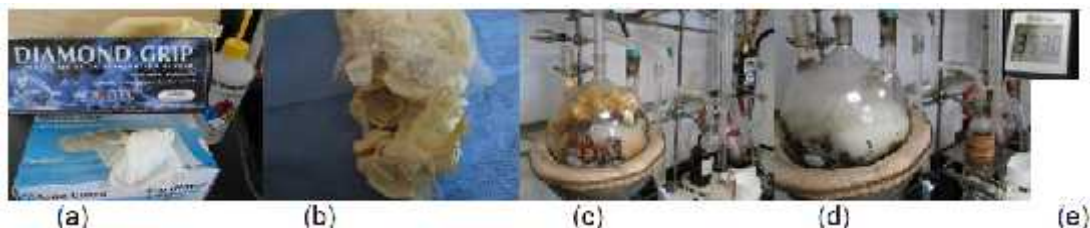
One-tenth to one microliter of each sample was injected into GC-MS by AOC-20i auto-sampler. The autosampler was set for three rinses before and after injection with a mixture of methanol/water, 90/10, v:v, and two rinses with the sample before injection. The plunger speed and syringe speed were set at high.

The MS program consisted of the scanning masses $15 < M/z < 350$; scanning time began from 0.4 min and ended after 35 minutes. The identities of chemicals were established by the aid of the automatic NIST library search. Among the suggested structures, the one that was better matched to the fragmentations pattern, consistent with boiling point and retention time of the compound was selected.

2.3 Pyrolysis Procedures

156 pairs of used LEGs weighted 879.8 g (Fig 1b) were placed into the reactor (Figure 1c). The end of a stainless steel type K thermistor was placed into the bottom of the three-necked 5-L flask (T1) to measure the decomposition temperature, another thermistor placed into the entrance of the side-arm distilling head (T2) to measure the temperature of the gases that left the reactor, and the third thermistor was placed at the exit of the Claisen adaptor to record the temperature of volatiles that left the collection funnel and condensed into the next receiver (T3, Figure 1c). Table 1 shows the stages of heating and decomposition process of LEGs. At 253°C vapors resulting of decomposing of LEGs were filled up the flask, air condenser, and the other flasks. The first drop of condensate (97°C) was collected into the recipient graduated funnel when the melt temperature reached 488°C. The drops at the time of condensation were clear liquid but when they reach to the bottom of the container the color was changed from bright yellow to dark green. By passing time the color of liquid becomes darker.

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Figure 1. Step-by-step illustration of decomposition process of LEGs: (a) LEGs before use, (b) LEGs collected during one year (2012); (c) LEGs loaded in the reactor; (d); the reactor at 393°C (e) the Thermolysis reading by a digital thermometer (T1).

Table 1. The thermal history of the reactor.

Temperature (°C)			Observation, Remarks and Comments
T1	T2	T3	
253	22.3	22	Smokey vapor started appearing, gloves started melting
475.2	34.5	25.2	Gloves began to melt vigorously and rapidly into gases
488.0	91.6	48.1	1st drop of liquid was observed at the collection point.
374.5	79.8	43.8	The contents of reaction flask were smoldering black.
382.9	89.5	60.6	The temperature increased steadily.
393.7	93.5	67.8	Sample 1 was collected
436.8	93..5	33.2	Sample 2 was collected
366	79	29	Final reading

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At this moment, the pressure of gases opened the joints, the liquids and uncondensed vapors were leaking out from the joints of Claisen adaptor; therefore, the reaction was stopped. 30 days later the needle like crystals were observed inside the reaction flask (Fig 2a). Some of the gloves were not decomposed yet but covered by the black residuals of the decomposed ones. Some of the materials leaked out of the joints were solidified around the joints with a pale color (Fig 2b and c). The solid was slightly soluble in acetone, soluble in methanol and boiling water. The solution was acidic. The pyrolysis was resumed after the joints were cleaned. Table 2 summarizes the results of second attempt to pyrolysis.



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Figure 2. Step-by-step illustration of decomposition process of LEG: (a) The white needle shape crystals grown in tope of the residues. (b) Accumulation of solids out of the joints. (c) A sample of the solids. (d) The setup. (e) The condenser with pale-yellow solids

Table 2. Thermal History of the reactor: second time pyrolysis

Time	Temperature (°C)	Comments
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	<u>T 1</u>	<u>T 2</u>	<u>T 3</u>	
11:00	152	25	25	The vapor and liquid equilibrium established inside of main flask
11:10	355	48	25	Vapor raising out of the reactor
11:13	355	74	25.7	The first drop of liquid was condensed near to the thermometer 1.
11:18	355	93	25.8	Vapors were condensing, flowing toward the gravity direction in air condenser. Their color was pail-yellow; however, the accumulated liquid in the funnel was dark black.

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194 The reaction was stopped since unusually high vapor pressure opened the joints and the
 195 solids were deposited in and outsides of them.
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197 ***Continuation of Reaction (third time)***

198 The collection parts of the system were cleaned dried prior to resuming the pyrolysis. The
 199 pyrolysis lasted ~ 5 hours, the pyrolysis was discontinued when the cloud of vapors was
 200 solidified around the neck of the reaction vessel. Table 3 shows the steps of the pyrolysis.
 201 At the beginning all the thermometers (T1, T2, and T3) readings were 23.0°C as was the
 202 room temperature. After six minutes of heating, a dark steam filled the flask then the argon
 203 gas valve was turned on (T1's reading was at 25.6° C; this indicates that the thermistor is not
 204 touching the bottom of the flask) (Fig 1c). After a period of 14 minutes the temperature of T1
 205 increased to 89° C, while T2's temperature was recorded at 51° C; during this period, clouds
 206 of vapor travelled through the air-condenser and first drops of liquid appeared around the
 207 road of the steam in the air condenser. After a period of fifteen minutes the first drop of liquid
 208 was observed in the funnel (Fig 4b), and T2 readings were constant, recorded 51° C. The
 209 initial sample collected was clear yellow in color and part of the liquid was solidified around
 210 the glass funnel. After few hours, the collected liquid divided into three phases, organic,
 211 aqueous, and solid crystals, (Fig 4d and e).
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Figure 3. Step-by-step illustration of decomposition process of LEGs (a) Solids deposited in the condenser, (b) and (c) Magnification of selected sections of (a), (d); crystallization of solids in the collection funnel, (e) deposit of greenish solids, (f) deposit of reddish solids, (g) deposit of yellow solids

Although, solid deposition in the air-condenser nearly blocked it, however the incoming distilled dissolved most of the solids and moved them into samples (Fig 3a to d). In the next step, a greenish solid filled the condenser but most of it was washed away by distillates (Fig 3e). After it, a reddish solid filled the path then it was washed away by coming distillates (Fig 3f). At the end a dark yellow solid remained in the condenser and the path of liquid (Fig 3 g).

As soon as a sample was collected, it was taken for GC-MS analysis, if the machine was busy in previous sample, then it was queued into auto-sampler to be processed as soon as possible. The first sample (sample 3) was collected at the condensing temperature of 57°C. The second sample (sample 4) were collected when the temperature of T1 and T2 increased to 186° C and 86° C, respectively, the T3's temperature was 23.3° C. Table 1 shows the time and amount of sample collected. Noticeable changes in the color of the solids were observed: change from a clear yellow (fig 4a-4d) to a darkish green (Fig 4e).



Fig 4. Results of pyrolysis of LEGs: (a) liquid condensed in the second flask, (b) The apparent of the first sample collected in the graduated funnel, (c) eleven samples collected from pyrolysis of LEGs, (d) Magnification of the appearance of samples 3, 4 and 5. (e) Sample 1 after 3 hours; it divides into three phases, organic, aqueous, and solid.

Some of the volatiles materials in conjunction with non-volatiles were condensed in the second container (Fig 4a). A close examination of the liquid indicated it was two phases: aqueous and organic. Later on, when we examined again the samples, it was composed of three phase of organic, aqueous, and solid (Fig 4f).

245 Table 3. Thermal History of the reactor: Continuation of pyrolysis and sampling (third
246 time)

Time	T1 (°C)	T2(°C)	T3(°C)	Observations
0	23	23	23	
10	42	23	23	Dark steam filled the 5L flask
14	89	51	23	Steam condensation
15	120	59	23	First drop of liquid
16.5	153	73	23	Sample 3 (6.87g)
23	244	107	23.6	Sample 3 (g)
32	328	112	37	Sample 4 (12.4g)
35	350	117	34	Sample 5(19.82g)
39		123	34	Sample 6 (14g)
42	388	140	32	Sample 7(10.97g)
51	402	130	28	Sample 8(12.77g)
56	395	134	28	Sample 9(16.92g)
65	396	147	27	Sample 10 (11.64g)
72		143	28	Sample 11 (12.5g)
90	385	86		Liquids in third flask was collected, Volatile Sample (13.26 g)
107	385	54	24	Sample 13 (9.75g)
155	414	71	23.9	Sample 14 (13.5g)
260	410	66	23.1	Sample 15 (16.67g)
297	435	175	23.9	Sample 16 (5 g)

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248 ***The Extraction with Boiling Water.***

249 The solid deposited in condenser during the pyrolysis was soluble in boiling water.
250 Therefore, extraction of the remains with boiling water may result in removing the solids. For
251 this, 100 mL of distilled water added to the reaction flask boiled for 10 min then filtered; 75
252 mL of hot filtrate was recovered. The rest of water was absorbed into remnants of the
253 pyrolysis. In the next day, a small amount of colorless crystals were visible on the walls and
254 on top filtrate. By filtration, some greenish (~100 mg) fiber-like materials were recovered (Fig
255 6a). Therefore, the amounts of boiling-water soluble materials were very low which indicated
256 those solids were trapped in the polymer network; they were liberated after the pyrolysis of
257 the polymeric network. Thus those organic acids and ester are not free and extractable prior
258 to pyrolysis which removes of the network.

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260 ***Continuation of the Pyrolysis.***

261 The condensers and receivers were washed well with methanol/water, 90/10, (v:v) then
262 reassembled. The heater set on 6 (scale of 1 to 10). After recovering 50 mL of water (with a
263 few mL of organic on top of it) the receiver for Sample B was placed under the funnel. Six
264 samples were collected (Fig 5 B-G). At the beginning the distillates were colorless with small
265 amount of organic layer on top (Fig 5 B and C). By advancing the pyrolysis, the amount of
266 aqueous layer decreased and the color changed. At the end the color of the sample was
267 dark red (Fig 5 samples E to G).

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Fig 5. The samples collected after aqueous extractions of reaction flask.

During sample E collection, the condenser filled with reddish solids. Most of these solids were dissolved in the distillates during the collection of samples E to G. At the end of pyrolysis at $T_1 = 620^\circ\text{C}$ little solids were remains in the condensers and the path (Fig H)

Table 4. Thermal History of the reactor: Continuation of pyrolysis and sampling (fourth time)

Time	T1	T2	T3	Observations
0:00	25.7	27.8	27.7	Initial temperatures
0:14	82.7	31.3	28.1	Condensation began to appear around the neck of reaction flask
0:18	105.1	51.8	28.1	H ₂ O droplets appeared in the condenser.
0:22	117.9	86.3	28.2	First drops of H ₂ O began to condense in the graduated funnel
0:28	121.3	97.1	28.9	H ₂ O droplets appeared by T3
0:42	121.6	97.1	39.4	25ml of H ₂ O was collected (Sample A)
1:00	121.8	96.8	30.1	45ml of H ₂ O was collected and some organics were visible in the beaker as well. The heat intensity was increased from 6 to 8
1:14	123.3	109.2	51.7	Over 75 mL of H ₂ O and organics was collected. Sample B was placed
1:36	181.5	114.5	41.4	Sample B's container was collected (20.09 g) and Sample C was placed
1:50	299.9	106.2	31.4	Yellow like crystalline solids were forming around the condenser
1:56	353.9	97.8	30.8	Sample C's container was collected (16.54 g) and Sample D was placed
2:00	388.3	87.9	29.7	Sample B and C's composition and color was noted to be similar. Both being a clouded light yellow solid like substance, with a light reddish brown liquid settling on the top. Sample C had slight solid formation around the container.
2:18	459.8	60.8	29.0	No liquid appeared to be coming out, solid formations was observed around the neck of flasks and condenser.
2:26	466.3	71.6	28.9	The solid precipitated around condenser appeared to be bright yellow in color
2:36	482.7	69.7	28.9	Sample D's flask was filled with $\frac{1}{4}$ liquid similar to that of Sample B and C
2:40	488.1	73.1	28.7	Heat intensity was increased from 8 to the maximum 10
2:44	490.5	192.9	28.7	Vigorous clouds of vapor began to rise from the 3 necked round bottom flask and travel down the condenser. Sample D's flask was collected (8.21 g) and Sample E was placed

2:48	495.0	277.0	32.2	The solid formation began to change color from a yellow to a vibrant red orange as the vapors continued to emit from the reaction flask. The vapors continued to emit from the flask vigorously. Sample E's flask was collected (16.66 g) and Sample F was placed
2:50	498.1	277.4	35.6	The heat intensity was decreased from the maximum to 9
2:52	506.1	271.8	36.6	Solid condensate and vapors continued to form as described previously
2:58	525.1	236.2	32.1	Sample F's flask was collected (17.93) and Sample G was placed
3:06	548.4	221.6	30.5	Sample G's flask was collected (18.02 g) and Sample H was placed
3:14	570.5	184.9	30.5	The formation of the crystalline solids were seen throughout the distillation system
3:28	614.4	135.8	35.3	An aliquot of Sample E (Sample 44) was taken for GC-MS analyzes
3:32	616.3	130.0	29.9	Sample H's flask was collected (14.52 g) and Sample I was placed
3:38	618.2	115.0	30.0	Sample I was collected (1.50 g) and the system was turned off due to the observation that no more liquid was coming from the system

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278 **3. RESULTS AND DISCUSSION**

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280 **3.1 Thermogravimetric Analysis**

281 About 12 mg of a LEG was cut into small pieces that can fit into the TGA pan (Fig 6a). The
 282 initial attempt was a heating scan from 50°C to 600°C under nitrogen. The end product has
 283 grey color and contained dark chunks (Fig 6b) which was indication of incomplete
 284 decomposition. The next heating ramp was from 50°C to 800°C, which resulted in white solid
 285 end products (Fig 6c).
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288 Fig 6. Thermogravimetric analysis: (a) pan loaded with 12 mg of LEG, (b) the remains after
 289 heated to 600°C; (c) the products at 800°C, (d) alkaline pH of the aqueous solution of the
 290 ashes.
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292 Figure 7 shows the results of thermogravimetric studies of LEGs, both powdered and un-
 293 powdered. The thermal stability of both type of LEGs are very similar; the decomposition
 294 began around 350°C reaches the highest rate at 410°C. The decompositions reaction was
 295 complete at 500°C; the residues of powdered LEG (~30%) are much more than that of
 296 powder free sample LEG (~12%) as expected. A second stage of decomposition was

observed around 625°C for powder free LEG and 650° for powdered LEG. The resulted ashes were white in color (Fig 7c) soluble in water producing a strong basic solution (Fig 7d) which is property of active metal oxides. The thermogravimetric data affirms the observation in the reactor (Tables 1 to 4) in the sense that the reaction vessel temperature was below 400°C during the pyrolysis process.

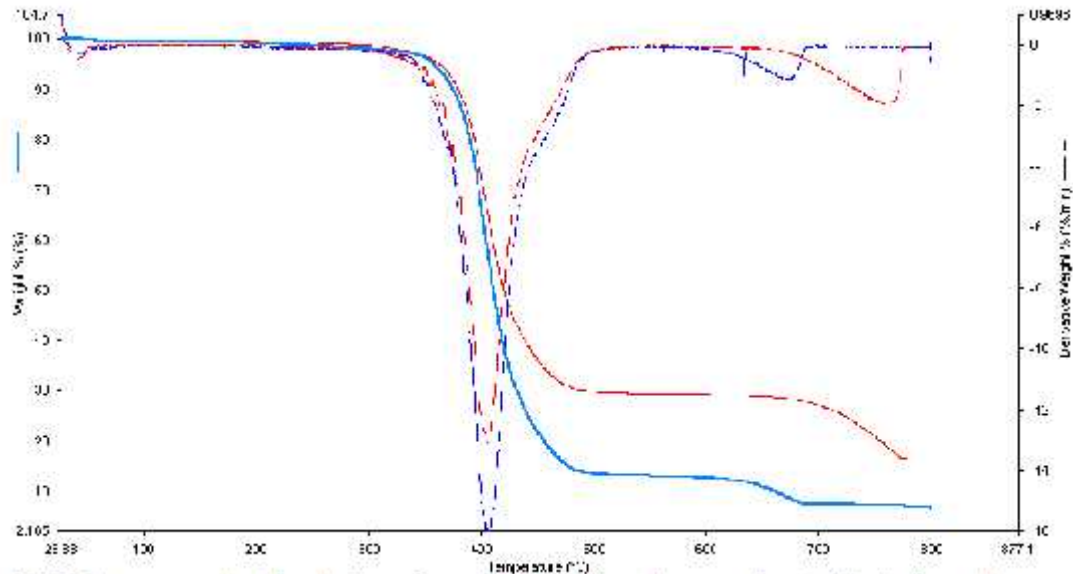


Fig 7. Thermogravimetric studies of powdered (red) and un-powdered (blue) gloves from 50°C of 800°C under 10 mL/min N₂ (g) with heating rate of 10°C/min.

3.2 Pyrolysis of LEGs

Fig 8 shows the total ion chromatograms of 9 of 25 samples of the pyrolysis products collected at various steps and temperatures. Below, the TIC will be annualized.

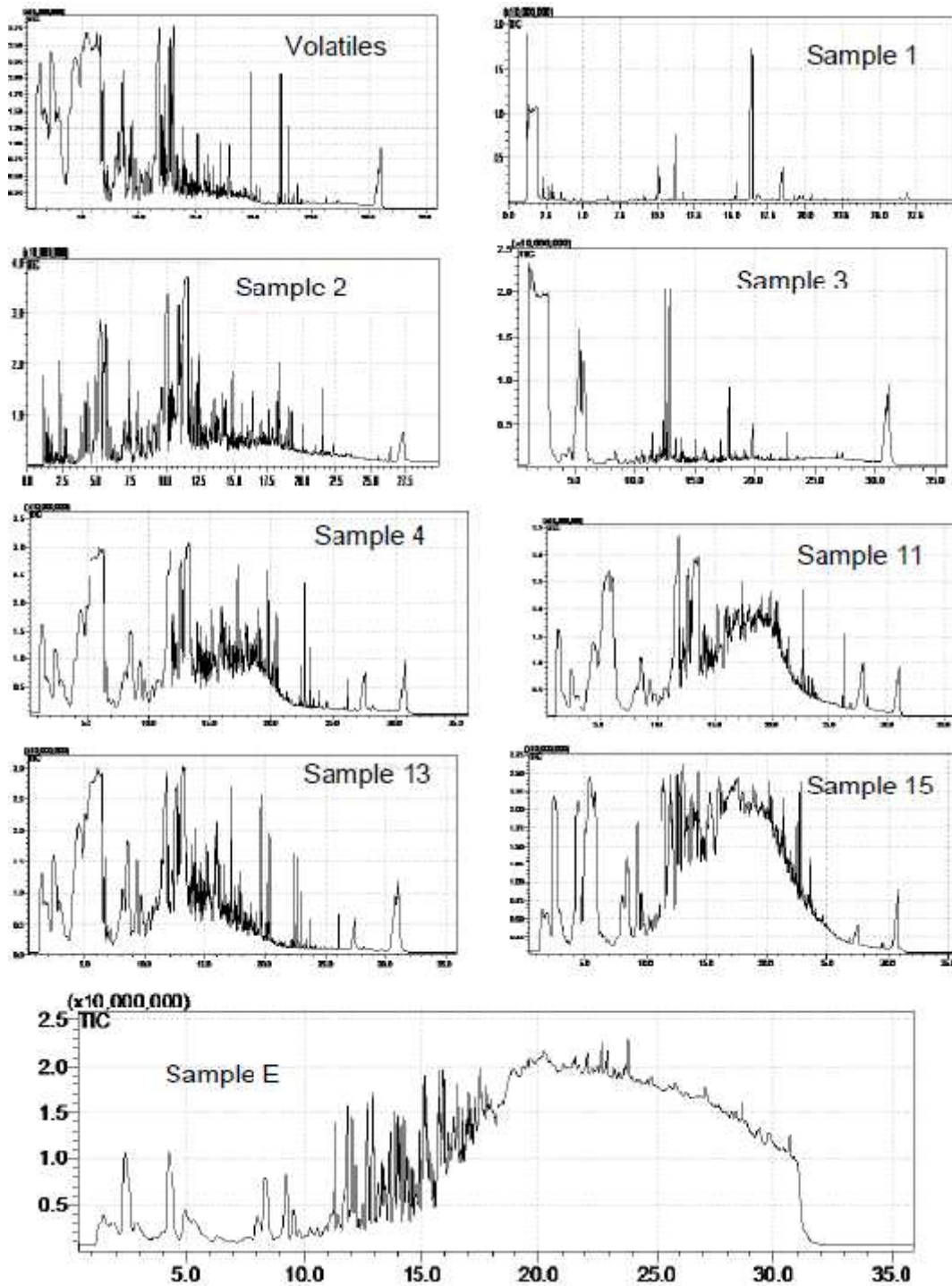


Figure 8. TIC of the representatives samples as described on the TIC and in the Tables 1, 3, and 4

The Most Volatile Sample

The most volatile sample consisted of the chemical that escaped the first collection container and accumulated in the second container which was kept cold in an ice-water bath (Fig 4a) and was equipped with a water condenser. As the TIC (Fig 8 Volatiles) showed the first peak at the chromatogram (1.150-1.358 min) was hydrogen chloride as expected; the next peak (1.358-1.558) represents a mixture of HCl and C₅ compounds, C₅H₁₀, then at the end of the peak (1.583-2.267 min) various isomers of C₆ compounds, C₆H₁₂, both cyclic and acyclic, with one saturated element, the broad peak located at 2.267-2.74min was benzene, C₆H₆, at 2.783-4.3 min C₇ compounds are visible such as 2,2-dimethylpentane (2.742Min) then heptene isomers (2.775-3.592 min), octene isomers appeared at 3.675 – 6.792 min while toluene, C₇H₈, is co-eluted with octenes (4.108-4.81 min). Then C₈ compounds with two unsaturated units were at 6.817-7.475 min. From 7.48 – 9 min the dimethyl benzene derivatives (C₈) with C₉ linear isomers were visible. The peak at 11.45-11.83 was hard to identify; the NIST library identifies it as 3-chlor-3-ethyl heptane with 88% similarity, however, the M/z = 91 may be indication of a benzylic cation or tropylium ion resulting from cleavage at benzylic carbon in the compound.

Another series of hydrocarbons detected between 10-15 min covering 3 major peaks 11.45-11.96, 12.56-12.68 min and 12.93-13.17 min, identifies as various isomers of straight chains C₁₁H₂₂ (192°C), C₁₁H₂₀ (bp 196), and C₁₁H₂₄ (bp 196°C)⁴⁴. Table 5 provides the least of major chemical in this sample. Also, a comparison between the mass of the compounds in the sample of volatiles and the MS in the NIST library is available (Fig 9).

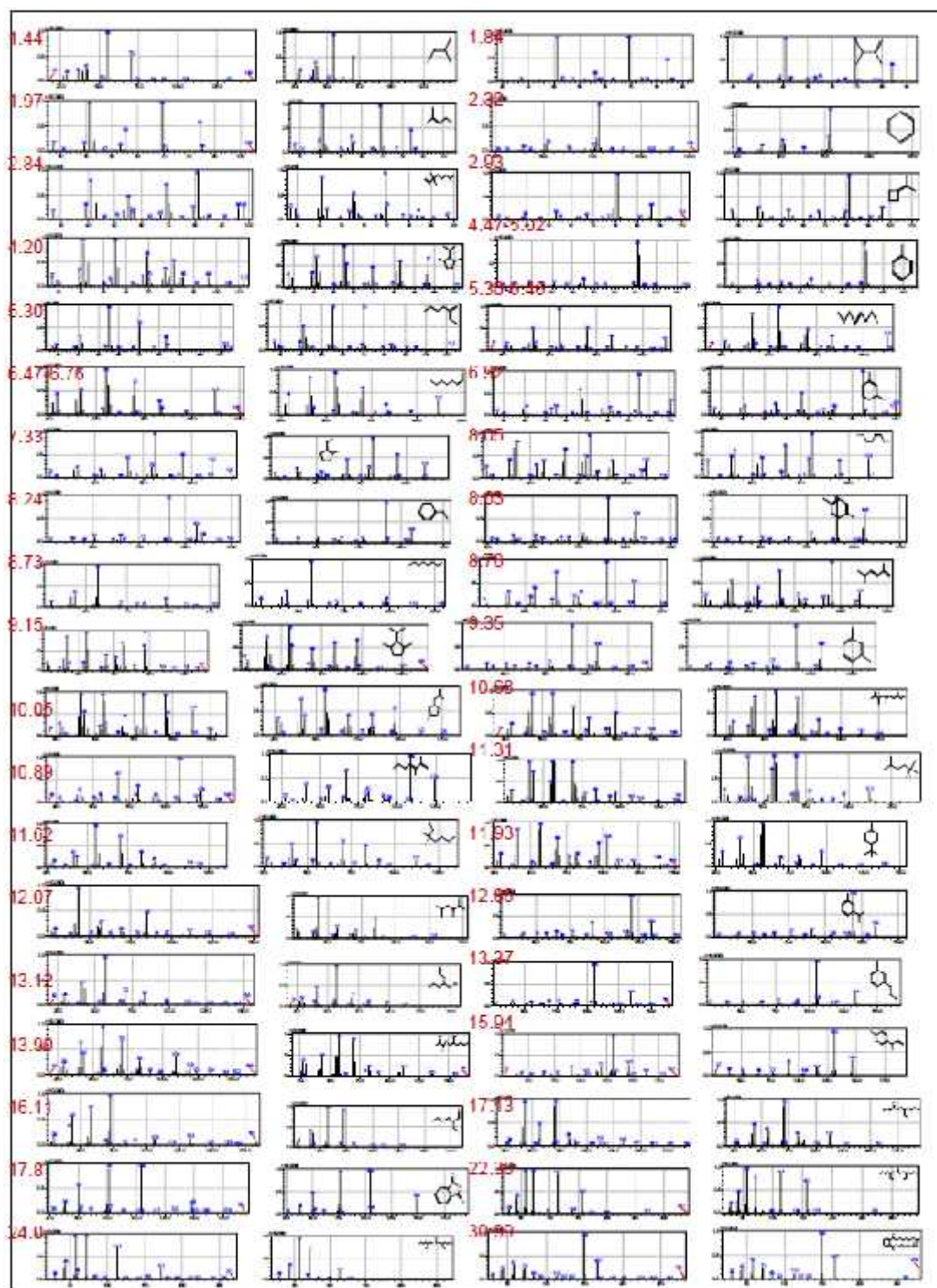


Fig 9. The MS of some picks of the most volatile sample (identified with their retention time, min) and the MS of most similar compound to the MS from NIST library

341

342 Table 5. The major chemical compositions of the most volatile sample of the pyrolysis.

Retention Time (min)			%	Name
Top	Start	End	Area	
1.451	1.117	1.575	4.70	Hydrogen chloride
1.607	1.575	1.683	0.86	Pentane, 2-methyl-
1.753	1.683	1.808	1.02	Cyclobutane, 1,2,3,4-tetramethyl-
1.853	1.808	1.883	0.63	3,7-Nonadien-2-one, 8-methyl-, (E)-
1.918	1.883	2.017	1.07	Furan, 2,3-dihydro-3-methyl-
2.034	2.017	2.142	0.85	Cyclopentene, 1-methyl-
2.207	2.142	2.250	0.72	Cyclopentene, 1-methyl-
2.334	2.250	2.383	1.67	Benzene
2.423	2.383	2.775	4.47	Heptane, 3,4-dimethyl-
2.853	2.775	2.900	0.98	1,4-Pentadiene, 3,3-dimethyl-
2.994	2.900	3.100	1.61	Cyclobutane, (1-methylethylidene)-
3.136	3.100	3.650	2.26	1,2-Benzenediol, O-dichloroacetyl-O'-(3-methylbut-2-enoyl)-
3.989	3.650	4.058	2.43	4-Octene, (Z)-
4.218	4.058	4.283	2.47	Toluene
4.447	4.283	4.550	3.37	Heptane, 4-ethyl-
4.559	4.550	4.825	3.26	Heptane, 3-methyl-
5.101	4.825	5.192	4.73	3-Heptene, 3-methyl-
5.447	5.192	6.042	12.06	Borane, diethylpropyl-
6.397	6.042	6.617	8.02	1,3,2-Dioxaborolan-4-one, 2-ethyl-
6.922	6.617	7.017	3.47	1,3-Dimethyl-1-cyclohexene
7.059	7.017	7.192	0.37	Bicyclo[3.1.1]heptan-3-one, 2,6,6-trimethyl-
7.248	7.192	7.492	0.41	1-Undecyne
7.557	7.492	7.617	0.14	Cyclohexene, 1,2-dimethyl-
8.002	7.617	8.142	1.36	2-Tetradecyne
8.256	8.142	8.342	0.93	Ethylbenzene
8.632	8.342	8.842	2.83	p-Xylene
9.169	8.842	9.242	0.80	Cyclopentane, 2-isopropyl-1,3-dimethyl-
9.363	9.242	9.492	0.88	o-Xylene
9.697	9.492	9.792	0.64	trans-2-Dodecen-1-ol, trifluoroacetate
9.873	9.792	10.042	0.30	Bicyclo[2.2.1]heptan-2-ol, 1,7,7-trimethyl-, (1S-endo)-
10.165	10.042	10.467	0.82	2-Undecyne
10.682	10.467	10.792	0.76	Furan, tetrahydro-2,2-dimethyl-5-(1-methylethyl)-
10.907	10.792	11.067	0.57	1,3-Hexadiene, 2,3,5-trimethyl-
11.327	11.067	11.392	1.09	Hexane, 2-chloro-2,5-dimethyl-
11.759	11.392	11.842	4.83	Heptane, 3-chloro-3-methyl-
11.891	11.842	11.992	0.65	3,5-Decadiene, 2,2-dimethyl-, (Z,Z)-
12.090	11.992	12.217	1.02	(1R,2R,3R,5S)-(-)-Isopinocampheol
12.267	12.217	12.417	0.63	6-Octenal, 3,7-dimethyl-
12.655	12.417	12.767	2.43	Pentane, 3,3-diethyl-
13.118	12.767	13.317	3.98	2-Propyl-1-pentanol
13.374	13.317	13.417	0.25	Benzene, 1-methyl-3-propyl-
13.470	13.417	13.592	0.36	3(10)-Caren-4-ol, acetoacetic acid ester
13.692	13.592	13.767	0.26	trans-.beta.-Terpinyl benzoate
14.035	13.767	14.167	0.99	6,7-Dimethyl-3,5,8a-tetrahydro-1H-2-benzopyran
14.269	14.167	14.517	0.57	1,7,7-Trimethyl-2-vinylbicyclo[2.2.1]hept-2-ene
14.564	14.517	14.617	0.15	(+)-3-Carene, 2-(acetylmethyl)-
14.783	14.617	15.017	0.59	Longipinocarveol, trans-

15.144	15.017	15.217	0.46	Acetic acid, 2-ethylhexyl ester
15.262	15.217	15.292	0.11	2-Methyl-7-endo-vinylbicyclo[4.2.0]oct-1(2)-ene
15.345	15.292	15.617	0.44	Benzene, 1,3-diethyl-5-methyl-
15.751	15.617	15.842	0.42	Benzene, 1,2-difluoro-4-[2-(4'-pentyl[1,1'-bicyclohexyl]-4-yl)ethyl]-
15.960	15.842	16.067	0.43	1H-Indene, 1-ethyl-2,3-dihydro-1-methyl-
16.130	16.067	16.217	0.23	Tetradecane, 1-chloro-
16.536	16.217	17.042	0.99	Cyclopentanol, 3,3,4-trimethyl-4-p-tolyl-, (R,R)-(+)-
17.142	17.042	17.292	0.38	Decane, 3,3,4-trimethyl-
17.428	17.292	17.592	0.35	Naphthalene, 1,2,3,4-tetrahydro-6,7-dimethyl-
17.811	17.592	17.867	0.58	1,2-Benzenedicarboxylic acid
17.919	17.867	18.042	0.21	Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl-
18.074	18.042	18.217	0.17	Benzene, (2,2-dimethyl-1-methylenepropyl)-
18.276	18.217	18.317	0.09	Tricyclo[20.8.0.0(7,16)]triacontane, 1(22),7(16)-diepoxy-
18.344	18.317	18.517	0.19	4-Hexyl-1-(7-methoxycarbonylheptyl)bicyclo[4.4.0]deca-2,5,7-triene
18.582	18.517	18.617	0.09	Isolongifolene, 9,10-dehydro-
18.789	18.617	18.917	0.28	1-Chloroeicosane
19.039	18.917	19.092	0.16	2- Bromopropionic acid, octyl ester
19.243	19.092	19.367	0.22	Naphthalene, 2,6-dimethyl-
19.476	19.367	19.592	0.16	Cyclopentanol, 3,3,4-trimethyl-4-p-tolyl-, (R,R)-(+)-
19.717	19.592	20.042	0.65	4-Methylnonanoic acid
20.073	20.042	20.217	0.09	2,9-Heptadecadiene-4,6-diyn-8-ol, (Z,E)-
20.338	20.217	20.442	0.14	Sulfurous acid, hexyl octyl ester
20.569	20.442	20.967	0.18	2,3-Dimethyldodecane
21.011	20.967	21.117	0.03	Bicyclo[4.1.0]heptan-2-ol, 1-phenyl-, endo-
21.318	21.117	21.367	0.06	Sulfurous acid, octadecyl pentyl ester
21.417	21.367	21.667	0.05	Cyclopropanecarboxylic acid, 2,2-dimethyl-3-(2-methyl-1-propenyl)-, cis-
21.717	21.667	21.917	0.03	Hexadecane, 2,6,10-trimethyl-
21.967	21.917	21.992	0.01	Octane, 1,1'-oxybis-
22.120	21.992	22.242	0.06	Silane, dimethyldi(2-ethylhexyloxy)
22.359	22.242	22.492	0.65	5,11-Diethyl-8-methyl-7,9-dioxapentadecane
22.645	22.492	22.792	0.06	Benzoic acid, 2-ethylhexyl ester
23.071	22.792	23.217	0.27	Sulfurous acid, di(2-ethylhexyl) ester
23.390	23.217	23.642	0.09	Sulfurous acid, 2-ethylhexyl pentyl ester
23.787	23.642	23.842	0.10	Sulfurous acid, 2-ethylhexyl pentyl ester
23.892	23.842	24.017	0.03	Pentadecane, 4-methyl-
24.119	24.017	24.217	0.05	Sulfurous acid, 2-ethylhexyl pentyl ester
24.242	24.217	24.317	0.02	2-Bromotetradecane
24.599	24.317	24.742	0.11	Diisooctyl adipate
25.011	24.742	25.267	0.11	Rhodopin
25.382	25.267	25.642	0.07	2-Ethylhexyl mercaptoacetate
25.792	25.642	26.017	0.07	Carbamodithioic acid, bis(phenylmethyl)-, 2,3,5,6-tetrafluoro-4-pyridinyl ester
26.342	26.017	26.442	0.08	Sulfurous acid, di(2-ethylhexyl) ester
26.852	26.442	27.092	0.08	Dodecanoic acid, isooctyl ester
27.337	27.092	27.542	0.09	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester
27.642	27.542	27.792	0.04	3-(n-Propylamino)-2,1-benzisothiazole
27.867	27.792	28.067	0.03	5-(7a-Isopropenyl-4,5-dimethyl-octahydroinden-4-yl)-3-methyl-pent-2-en-1-ol

28.394	28.067	28.542	0.05	Benzoic acid, 4-(dodecyloxy)-
28.617	28.542	28.867	0.02	dl-3Beta-hydroxy-d-homo-18-nor-5alpha,8alpha,14beta-androst-13(17a)-en-17-one
31.006	30.292	31.392	1.45	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester

Sample 1

Sample 1 was the first drops (head) collected, from the beginning of the pyrolysis reaction (383°C-393°C) and condensed below 94°C. The main component of the sample 1 was hydrogen chloride, HCl, and moisture (Fig 8 Sample 1) which appeared on chromatogram from 1.15 to 2.85 min.

As the TIC of sample 1 (Figure 8 sample 1) showed there were over 170 chemicals identified by the auto-research of GC-MS with very low concentration relative to HCl. Figure 10a shows the background or the baseline of the chromatogram at the initial time, these M/z are the ion of gasses that were dissolved in the sample; CO₂, (M/z = 44 Da), oxygen (M/z = 32 Da), NO (M/z = 30 Da), and N₂ (M/z = 28 Da). These low molar mass compounds produced from decomposition of gloves; dissolved in the sample, as also was reported by Williams et al [1]. The chromatogram of sample 1 showed two main compounds: one appears from 1.25 min to 2.45 min, with M/z 36 and 37 (Fig 11b) which has been identified as HCl, hydrogen chloride (Fig 11c). HCl, at room temperature, is a colorless gas, which forms white fumes of hydrochloric acid upon contact with atmospheric humidity as was observed at the beginning of the pyrolysis reaction (Fig 1d). HCl melts at -114.9 °C and boils at -85.06°C. It dissolves well in polar protic solvents such as water and alcohols and aprotic organics containing oxygen and nitrogen. Further analysis of TIC indicated that the pyrolysis liquids are rich in oxygenated compounds. The pH of sample 1 was >2 measured by pH-paper which confirmed strong acidity of the sample. HCl produced by decomposition of chlorinated polymers utilized to fabricate the gloves. One of such polymers is neoprene or polychloroprene, a family of synthetic rubbers that are produced by polymerization of chloroprene [4]. The chloroprene decomposed first to HCl and other chemicals as:

$[-CH_2-CCl=CH-CH_2-]_n(s) \rightarrow HCl(g) + \text{other chemicals}$

The other components of sample 1 were at 11.26 min 2-propyl-1-pentanol or 2-ethyl-1-hexanol or 6-methyl-3-undecane, phthalic anhydride which appeared at 16.4 min, and at 18.5 min phthalimide appeared besides saturated and unsaturated hydrocarbons.

Main other chemicals from the decomposition of neoprene are oligomers H-(CH)_n-H, such as methane, ethane, ethyne, propene, butadiene, and cyclic aromatic compounds resulting from secondary reaction of the decomposition products such as benzene and its derivatives, and other polycyclic compounds such as naphthalene and its derivatives as reported by other researchers [25]. Visual observation of the reactor indicated that the liquefied vapors were very reactive. At the beginning of the air-condenser they were colorless, when they reach to the end of condenser, the color changed, and within the liquid, solid crystals appeared. Table 6 shows 50 major chemicals identified by the NIST library in the sample.

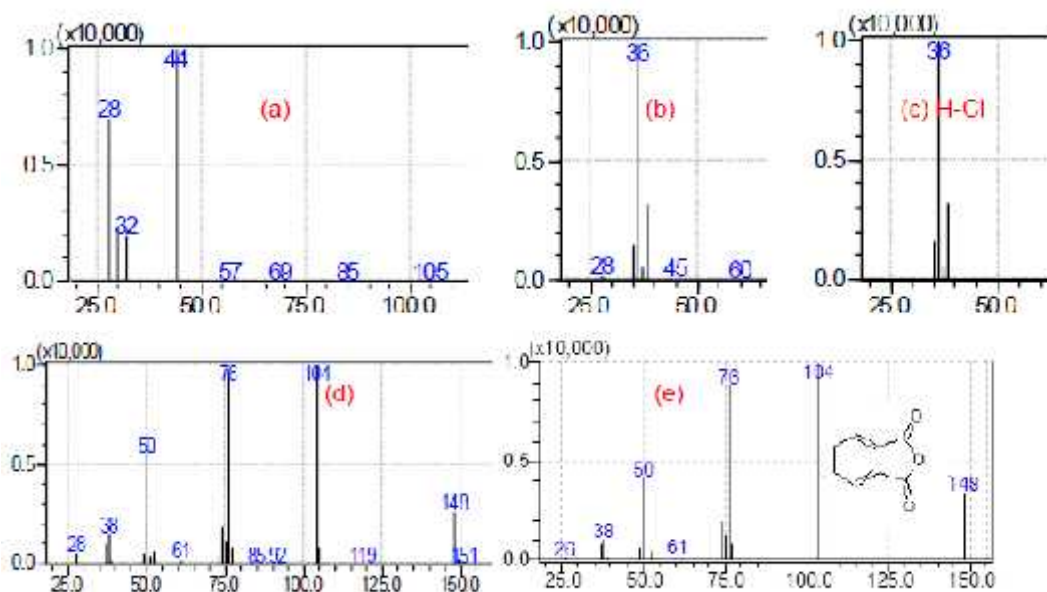


Fig 10. (a) A background scan at the beginning of TIC, (b) a scan from the peak appeared from 1.25 -1.75 min, (c) MS of HCl from NIST library, (d) a scan of compound appeared at 16.45 min, (e) a MS of phthalic anhydride from the NIST library.

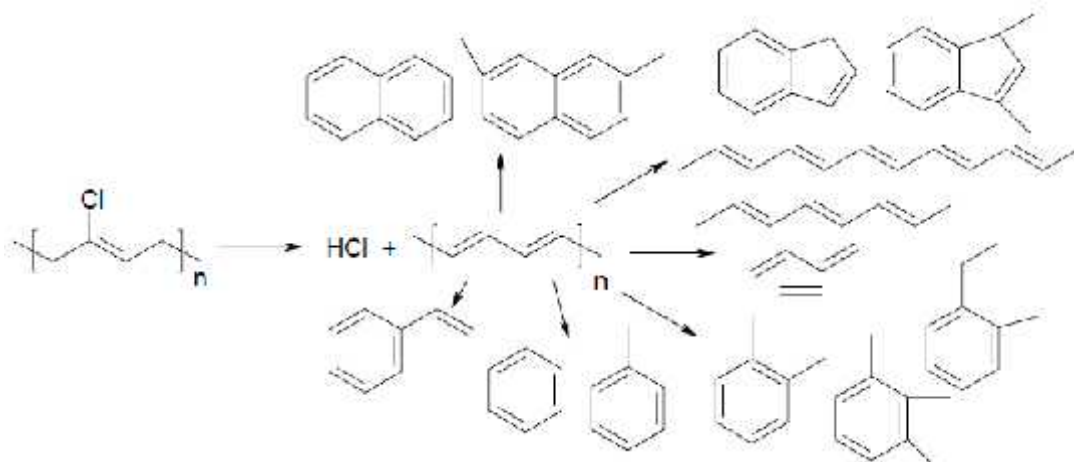
Table 6. Major chemicals identified in the sample 1 by GC-MS.

Retention Time (min)			Area %	Name
Top	Start	End		
1.141	1.108	2.22	52	Hydrogen chloride
2.269	2.225	2.558	1.23	2-Chloroethanol
2.675	2.650	2.792	0.48	1-Chloro-2-Propanol
2.860	2.792	2.950	0.61	1,4-Dioxane
2.984	2.950	3.067	0.24	2-Chloro-1-propanol
3.474	3.450	3.600	0.43	1,2-Ethanediol
3.692	3.600	3.775	0.10	2-ethoxy-ethanol
4.796	4.767	4.967	0.38	Cyclopentanone
6.031	5.967	6.133	0.10	Cyclotrisiloxane, hexamethyl-
6.686	6.633	6.808	0.23	Thiophene, tetrahydro-2-methyl-
8.412	8.383	8.450	0.08	2-Cyclopenten-1-one, 2-methyl-
8.607	8.450	8.675	0.27	3-Nitropropanoic acid
8.712	8.675	8.775	0.06	2-Ethyl-4,6-dimethyltetrahydropyran
9.048	9.017	9.117	0.15	Furan, 2,5-diethyltetrahydro-
9.148	9.117	9.217	0.11	Furan, 2,5-diethyltetrahydro-
9.558	9.533	9.683	0.06	Formamide, N,N-diethyl-
9.890	9.833	9.942	0.24	2-Nonanol, 5-ethyl-
9.992	9.942	10.017	0.15	Fumaric acid, 3-fluorophenyl hexadecyl ester
10.055	10.017	10.133	1.42	Ethanol, 2-(2-chloroethoxy)-
10.180	10.133	10.242	0.38	Propanoic acid, 3-chloro-
10.758	10.658	10.792	0.05	1,2-Epoxyundecane
10.891	10.792	10.992	0.10	Ethanol, 2-(2-ethoxyethoxy)-

11.262	11.208	11.392	2.11	2-Propyl-1-pentanol
11.786	11.725	11.892	0.32	2(3H)-Furanone, 5-ethyldihydro-
13.183	13.117	13.250	0.05	2,5-Pyrrolidinedione
13.922	13.758	13.992	0.16	Benzoic acid
14.880	14.833	14.925	0.08	2-Heptanol, 6-methyl-
15.027	14.983	15.050	0.05	Cyclohexane, 1-methyl-2-propyl-
15.249	15.100	15.358	0.82	3-Nitro-2-butanol
16.448	16.083	16.575	21.78	Phthalic anhydride
16.797	16.733	16.825	0.13	1(3H)-Isobenzofuranone
16.919	16.825	16.967	0.27	Hexanedioic acid
18.464	18.283	18.600	3.43	Phthalimide
19.185	19.125	19.242	0.15	Ethanol, 2-[2-(2-chloroethoxy)ethoxy]-
19.508	19.450	19.533	0.12	Bis(2-(2-chloroethoxy)ethyl)ether
19.568	19.533	19.617	0.19	Phthalic acid, di-(1-hexen-5-yl) ester
19.789	19.617	19.842	0.41	Phthalimidine
20.354	20.258	20.450	0.30	Phthalic acid, di-(1-hexen-5-yl) ester
21.434	21.375	21.517	0.07	2-Acetylbenzoic acid
22.554	22.500	22.617	0.06	Ethanol, 2-[2-(2-chloroethoxy)ethoxy]-
22.830	22.783	22.883	0.06	Bis(2-(2-chloroethoxy)ethyl)ether
24.869	24.792	24.992	0.12	Heneicosane
26.357	26.242	26.483	0.24	Benzenemethanamine, N-hydroxy-N-(phenylmethyl)-
26.867	26.633	27.108	1.46	1,2-Propanediol, 3-benzyloxy-1,2-diacetyl-
29.866	29.725	29.983	0.07	Heneicosane

Sample 2

Table 7 shows 50 major chemicals identified in the sample 2. Sample 2 contains a smaller amount of HCl compared to sample 1 (Fig 8 Sample 2). This can be interpreted by the mechanism of pyrolysis of chlorinated polymers which occurs in various stages; the first step is emission of HCl and production of unsaturated polymers [23]. Then these unsaturated polymers decompose to other hydrocarbons. Therefore, most of HCl were volatilized and left the reactor prior and during the collection of first sample. The major chemicals of sample 2 were: at 2.27 min identified as benzene. From 4.75 min to 5.89 min the isomers of octane were identified: at 5.27 min 3-ethyl-2-hexene as showed by MS (Fig 11) at 5.65 min 3-methyl-2-heptene and at 5.79 min 2-octene. The next major chemical at 7.4 min is another isomer of C₈, xylene. At 8.25 min nonane was identified. At 8.7 min the C₁₀ isomers began to appear. Also, some chlorinated compounds are visible; the peak at 10.05 min on the chromatogram was identified as 3-chloro-3-methyl-heptane. The MS of 3-chloro-heptane and 2-ethyl-hexanol are very similar to each other. At 11.0 min was also another chlorinated compound, 1-chloro-2-ethyl-heptane, and at 11.49 min 2-ethyl-hexanol either/or 6-methyl-3-undecene was identified. At 11.9 min it was also a C₁₀ isomer and was identified as 3-carene. The reaction below (Reaction 1) shows the production root of some of the chemicals produced from pyrolysis of neoprene.



Reaction1. Schematic representation of some chemicals resulting from decomposition of neoprene.

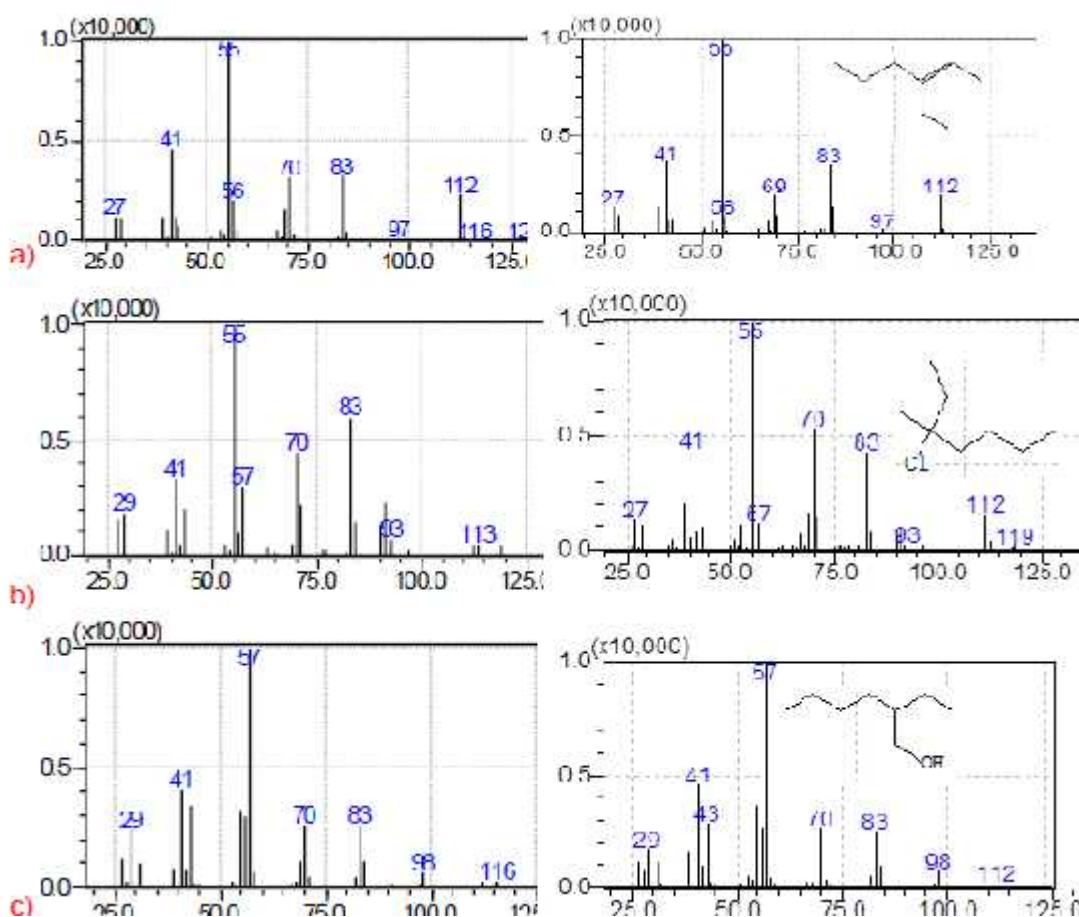


Fig 11. MS of the major compounds in sample 2 compared with the MS of the most similar compound from NIST library.

414 Table 7. 50 Major chemicals identified in the sample 2 by GC-MS.

Retention Time (min)			Area %	Name
Top	Start	End		
1.145	1.117	1.192	1.23	Hydrogen chloride
1.383	1.367	1.400	0.24	1,3-Butadiene, 2-methyl-
2.267	2.225	2.342	2.16	Benzene
2.711	2.650	2.750	0.51	Heptane
4.311	4.208	4.383	2.28	Heptane, 3-methyl-
4.939	4.842	5.067	3.69	3-Ethyl-3-hexene
5.359	5.125	5.442	11.54	4-Octene, (E)-
5.680	5.600	5.708	4.90	2-Heptene, 3-methyl-
5.805	5.708	5.833	2.91	2-Octene
6.969	6.858	7.033	1.31	Cyclohexane, 1,2-bis(methylene)-
7.406	7.325	7.450	2.69	p-Xylene
7.543	7.450	7.617	1.06	2,4-Hexadiene, 2,3-dimethyl-
7.899	7.850	7.942	0.85	Dichloroacetic acid, 1-cyclopentylethyl ester
8.037	7.942	8.100	1.58	p-Xylene
9.367	9.317	9.592	1.57	1,5,5-Trimethyl-6-methylene-cyclohexene
9.707	9.592	9.800	4.36	trans-2-Undecen-1-ol
10.008	9.800	10.158	15.89	Heptane, 3-chloro-3-methyl-
10.179	10.158	10.217	0.52	Bicyclo[2.2.1]heptane-2,3-dione, 1,7,7-trimethyl-, (1S)-
10.272	10.217	10.292	0.85	Benzene, 1-ethyl-3-methyl-
10.332	10.292	10.375	0.73	Bicyclo[4.1.0]heptane, 3,7,7-trimethyl-, (1.alpha.,3.alpha.,6.alpha.)-
10.492	10.475	10.517	0.50	1,1,4-Trimethylcyclohexane
10.543	10.517	10.608	1.05	Benzene, 1,3,5-trimethyl-
11.000	10.900	11.075	6.97	Heptane, 3-(chloromethyl)-
11.105	11.075	11.133	1.44	Bicyclo[4.1.0]hept-2-ene, 3,7,7-trimethyl-
11.208	11.142	11.225	1.86	Benzene, 1-ethyl-4-methyl-
11.255	11.225	11.275	1.37	Benzene, 1-methyl-2-(1-methylethyl)-
11.671	11.183	11.833	12.24	
11.756	11.725	11.808	0.43	Bicyclo[3.1.1]hept-2-ene-2-ethanol, 6,6-dimethyl-
11.931	11.892	12.008	1.49	1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-
12.131	12.100	12.200	0.68	Cyclohexene, 4-methyl-1-(1-methylethenyl)-
12.323	12.267	12.383	1.27	2-Bromopropionic acid, 2-ethylhexyl ester
12.449	12.383	12.467	1.93	1,3-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-
12.500	12.467	12.575	1.67	Benzene, 1-ethenyl-3,5-dimethyl-
12.639	12.600	12.675	0.60	Tridecane
13.390	13.367	13.425	0.44	Benzene, 1-methyl-2-(2-propenyl)-
13.542	13.425	13.567	0.87	Acetic acid, 2-ethylhexyl ester
13.591	13.567	13.650	0.79	Benzene, 1-ethenyl-4-ethyl-
14.204	14.158	14.267	1.01	Azulene
14.344	14.267	14.375	0.65	Octane, 3,4,5,6-tetramethyl-
14.405	14.375	14.458	0.72	Benzene, 1-methyl-4-(1-methyl-2-propenyl)-
14.871	14.800	14.908	1.54	Bicyclo[3.1.1]heptane, 6,6-dimethyl-3-methylene-
15.615	15.583	15.650	0.49	n-Butyric acid 2-ethylhexyl ester
16.355	16.217	16.375	1.61	Phthalic anhydride
17.613	17.575	17.650	0.44	Pentanoic acid, 2-ethylhexyl ester

18.172	18.133	18.208	0.50	3-Chloropropionic acid, 2-ethylhexyl ester
18.324	18.283	18.350	1.16	3-Hexanol, 3,5-dimethyl-
18.982	18.967	19.008	0.35	3-Heptanone, 2-methyl-
21.447	21.400	21.483	0.86	Benzoic acid, 2-ethylhexyl ester
26.386	26.208	26.583	0.18	Dodecanoic acid, isooctyl ester
27.396	26.583	28.108	1.80	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester

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Sample 3

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This sample was the first to be collected at third attempt to pyrolyze LEGs. Table 8 shows 50 of the major chemicals in the sample 3. Chromatogram of sample 3 (Fig 8 Sample 3) shows nine major compound, though the total number of chemicals in the sample exceed 250. The background at the initial time shows moisture ($M/z = 18$ in excess), nitrogen ($M/z = 28$), oxygen ($M/z = 32$) and argon ($M/z = 40$), the gases that were dissolved in the sample. The first peak (1.15-2.92 min) is a mixture of moisture ($M/z = 18\text{Da}$) and HCl ($M/z = 36\text{Da}$ and 38Da) or $(\text{H}_3\text{O}^+)\text{Cl}^-(\text{H}_2\text{O})_n$, as indicated in MS (Fig 12b). The major compound appeared at 5.433 min was identified as 4-octene (Fig 12c). At 12.52 min 5-methyl-2-decane on the chromatograph, then 12.76 min showed 2-ethyl-1,3-dimethylbenzene. The next compound was at 12.98 min 2-propylpent-1-ol or 2-ethyl-hex-1-ol or 6-methyl-3-undecene. The compound at 17.81 min was identified as phthalic anhydride and at 30.8 min diisooctyl phthalate and the last compound was identified as 1,2-benzenedicarboxylic acid, and ester at 30.94 min mono (2-ethylhexyl) phthalate. Fig 12 shows the MS of the major chemicals in the chromatogram compared with the MS of NIST library. The peak's RT also indicated on the MS.

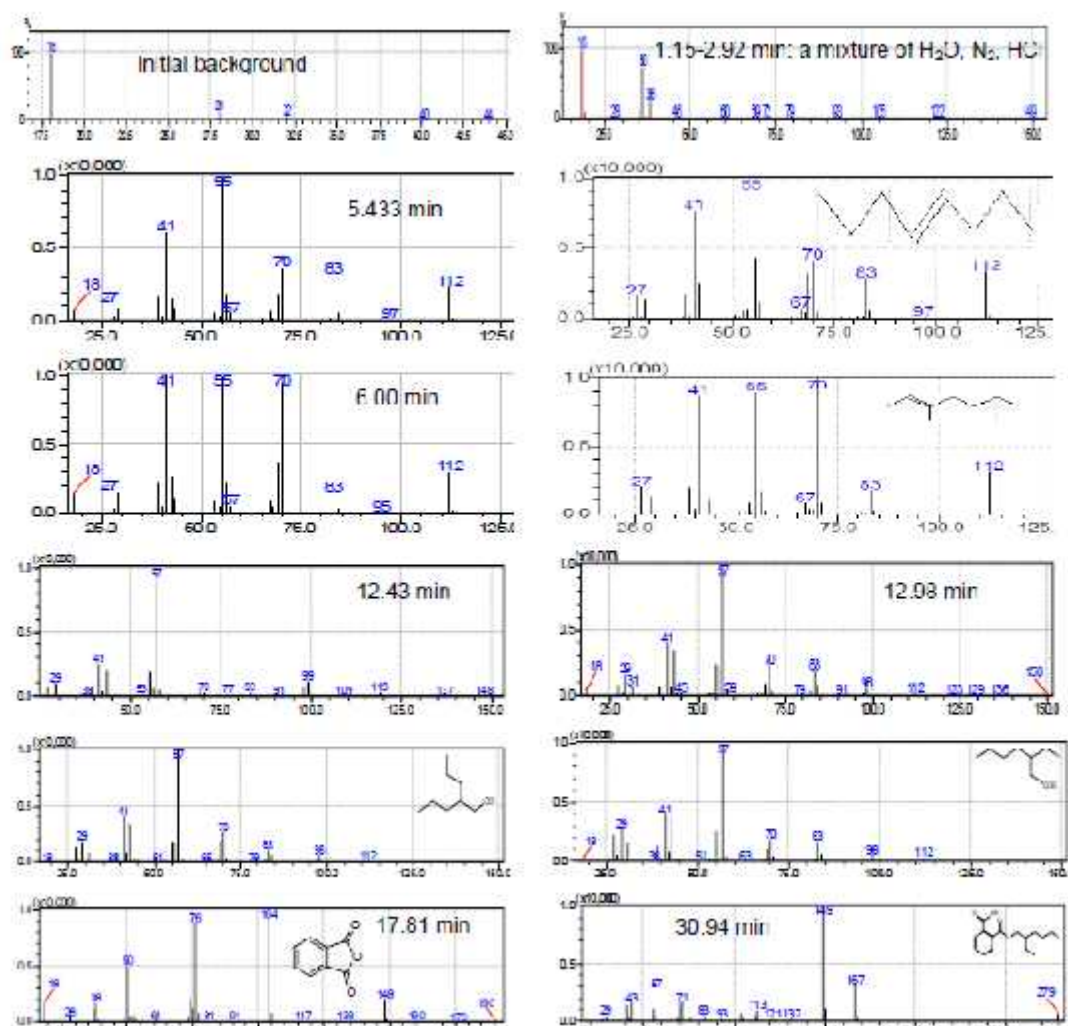


Figure 12 Chromatograph of major compounds in Sample 4

Table 8. 50 major chemicals identified in the liquid obtained by the pyrolysis of LEGs, sample 3

Retention Time (min)			Area %	Name
Top	Start	End		
1.178	1.142	2.8	40	Hydrogen chloride
4.015	3.667	4.192	0.63	3-Heptene, 3-methyl-
4.217	4.192	4.283	0.13	1,7-Dichloroheptane
4.502	4.283	4.775	1.05	4-octane
5.117	4.775	5.150	2.33	3-Heptene, 3-methyl-
5.428	5.150	5.692	10.03	3-Heptene, 3-methyl-
6.432	6.267	6.867	0.29	Cyclohexene, 3,5-dimethyl-
7.002	6.867	7.317	0.04	4,6-di-tert-Butylresorcinol
8.142	7.967	8.267	0.18	Ethylbenzene

8.417	8.267	8.792	0.50	o-Xylene
8.942	8.792	8.992	0.02	4-Nonene
9.618	9.417	9.742	0.10	3-Tridecene
10.128	9.992	10.417	0.18	2-Ethyl-4,6-dimethyltetrahydropyran
10.524	10.417	10.742	0.36	Furan, 2,5-diethyltetrahydro-
10.827	10.742	10.992	0.16	1,3-Hexadiene, 2,3,5-trimethyl-
11.466	10.992	11.692	0.79	Heptane, 3-chloro-3-methyl-
11.842	11.692	11.917	0.23	Bicyclo[4.1.0]heptane, 3,7,7-trimethyl-
12.192	12.142	12.367	0.29	Octane, 2-chloro-
12.536	12.367	12.592	1.89	Pentane, 3,3-diethyl- or 2,3,5-trimethylheptane
12.974	12.842	13.242	2.56	2-Propyl-1-pentanol
13.625	13.542	13.792	0.09	Benzoic acid, 4-isopropenylcyclohexenylmethyl ester
13.886	13.792	13.942	0.21	Chloroacetic acid, 2-ethylhexyl ester
14.243	14.142	14.292	0.08	Bicyclo[4.1.0]heptane-7-methanol, 7-bromo-.alpha.-ethyl-, (1.alpha.,6.alpha.,7.alpha.)-
14.849	14.592	14.992	0.19	1-Decene, 10-bromo-
15.120	14.992	15.292	0.25	Acetic acid, 2-ethylhexyl ester
15.721	15.467	15.817	0.42	Benzoic acid
16.139	16.067	16.217	0.05	Bicyclo[2.2.1]heptane-1-carbonitrile, 4,7,7-trimethyl-3-oxo-
16.518	16.217	16.567	0.12	Trichloroacetic acid, 2-ethylhexyl ester
17.242	16.942	17.292	0.25	Benzene, (2-propynyloxy)-
17.432	17.292	17.517	0.11	Naphthalene, 2-methyl-
17.811	17.517	18.042	1.39	1,2-Benzenedicarboxylic acid
18.242	18.192	18.292	0.09	1(3H)-Isobenzofuranone
18.773	18.717	18.817	0.06	1-Iodo-2-methylundecane
19.238	18.867	19.367	0.38	Naphthalene, 1,7-dimethyl-
19.846	19.617	19.992	1.12	Phthalimide
20.846	20.717	20.917	0.07	Bis(2-(2-chloroethoxy)ethyl)ether
21.515	21.467	21.917	0.12	Fluorene, 2,4a-dihydro-
22.042	21.917	22.092	0.05	Benzene, 1,1'-(1,3-propanediyl)bis-
22.642	22.392	22.767	0.26	Benzoic acid, 2-ethylhexyl ester
23.117	23.067	23.167	0.04	1-Adamantanecarboxylic acid, 3-tetradecyl ester
23.192	23.167	23.217	0.02	Benzene, (1-ethyldodecyl)-
23.717	23.642	23.842	0.08	Pentafluoropropionic acid, dodecyl ester
24.523	24.367	24.742	0.23	Hexanedioic acid, dioctyl ester
25.667	25.542	25.817	0.14	6,7-Dimethyl-3,4-dihydro-1H-[1,4]diazepino[3,2,1-hi]indol-2-one
26.317	26.192	26.492	0.13	Xanthophyll
26.865	26.492	26.967	0.28	Dodecanoic acid, isooctyl ester
31.011	30.267	31.817	5.51	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester

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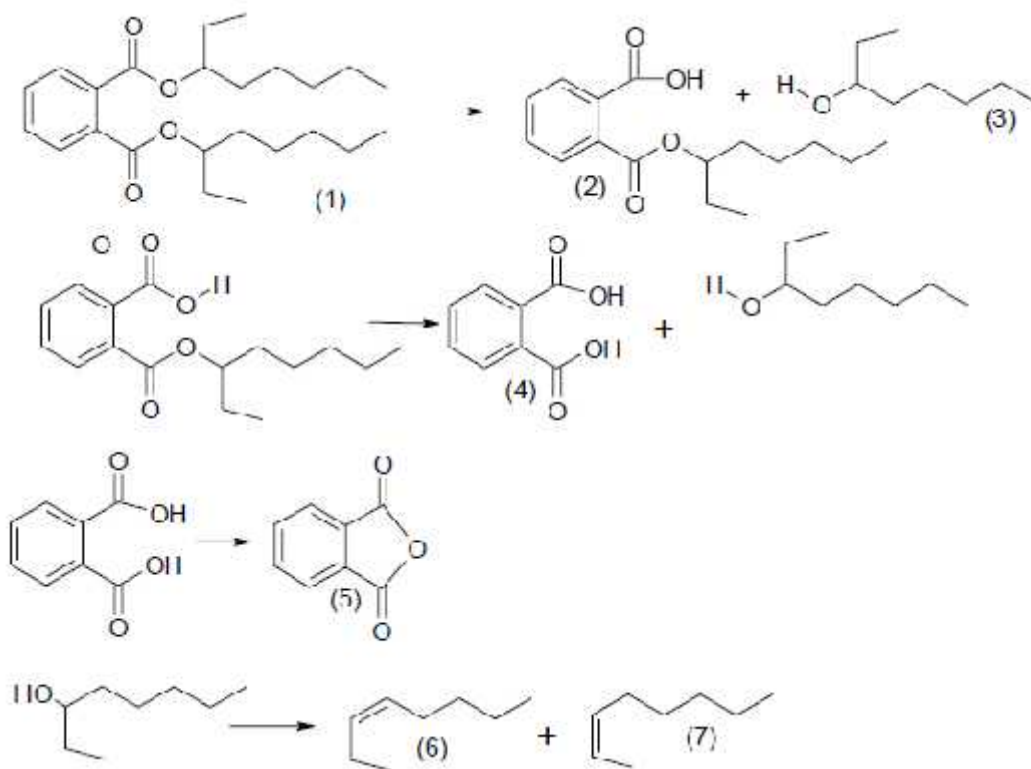
441 **Sample 4**

442 The chromatogram (Fig 9 Sample 4) shows at 1.16 min a mixture of water, HCl, and C₅
443 isomers. At 1.59 min the concentration of moisture and HCl decreased very much, however,
444 the C₅ compounds continue to elute, 1-pentene (mp 30°C) is visible, the mixture of pentene
445 and HCl make the library to recognize it as 2-chloropentane (bp 98°C) which must come at a

later retention time. At 2.0 min, hexene (bp 63°) has the highest concentrations (C_6 compounds) and 2.28, benzene (80°C) appeared, at 2.87 min C_7 isomers are visible. From 3.84 to 8.0 min C_8 isomers are identified (4-octene). After 8 min also the C_8 isomers are eluting; these isomers possessed more than one double bond for example the scan at 8.333 min identified as 3,5-octadiene. From 8.50 min we began to observe C_9 isomers for example scan at top of peak at 8.567 min identified as 3,5,5-trimethylcyclohexene. Xylenes (benzylic C_8) appeared from 8.633 to 9.10min. At 9.125 C_9 isomers began to appear, the scan on top of the peak at 9.242 min identified as 4-nonene. The peak at 9.50 min indicates the presence 1-ethenyl-3-methylene-cyclopentene. At 9.90 min 7-methyl-3-octene, and 2,4-dimethyl-2,4-heptadiene was appeared at 10.45-10.57min. From 10.88 to 10.58 min 2,5-diethyltetrahydrofuran and after it comes 2,2'-bioxepane, C_{10} isomers are visible after 11.3 min for example the scan at 11.30 min identified 2,6,6-trimethyl-bicyclo[3.1.1]heptane a C_{10} isomer. The one centered at 12.717 was 2,6,6-trimethylbicyclo[3.1.1]heptane $C_{10}H_{18}$, and the one at 13.0 was 4-bromoheptane $C_7H_{15}Br$; the lower section at 13.8 identified as 6,8-nonadien-2-one, 6-methyl-5-(1-methylethylidene) $C_{13}H_{20}O$. The peak at 13.21 to 13.66 was 2-propyl-1-pentanol or 2-ethyl-1-hexanol $C_8H_{18}O$ that their MS is very near to each other. The compound at 26.97 was isobutyl laurate dodecanoic acid $C_{16}H_{32}O_2$, the compound at 27.742 was 1-propylpentyl laurate $C_{20}H_{40}O_2$; and at 27.733 mono(2-ethylhexyl) phthalate $C_{16}H_{22}O_4$, at 27.983 eicosanoic acid, $C_{20}H_{40}O_2$, at 28.083 to 28.150 identified as 2,6-ditert-butyl-4-methylphenyl-1-(1-hydroxy-2-methylpropyl)cyclopropanecarboxylate $C_{23}H_{36}O_3$. The compound at 28.275 was identified as silane, dimethyl(2-propylphenoxy) butoxy- $C_{15}H_{26}O_2Si$, the compound at 28.267 to 28.457 was identified as Succinic acid, 2-ethylhexyl undecyl ester $C_{23}H_{44}O_4$, the compound at 29.150 was identified as (3-beta)- 14-methylcholest-7-en-3-ol $C_{28}H_{48}O$, the compound at 29.681 was identified as heptyl ester, toluic acid $C_{15}H_{22}O_2$, the compound at 30.492 was identified as n-tetracosane $C_{24}H_{50}$, the compound at 30.617 was identified as 2-ethylhexyl undecyl ester, fumaric acid $C_{23}H_{42}O_4$, the compound at 30.867 was identified as 2-chloroethyl decyl ester phthalic acid $C_{20}H_{29}ClO_4$

Sample 15

The appearance of the chromatograms of samples 5 to 14 were similar, therefore, the extended analysis of every sample is omitted. As the chromatogram (Fig 8) shows the sample 15 has higher concentrations of compounds eluted after 15 min RT. Decomposition of plasticizers derivative of phthalic acid such as di-(2-ethylhexyl)phthalate (Reaction 3, (1)) and polyesters may lead to compounds such as mono-(2-ethylhexyl)phthalate (Reaction 1, (2)), 2-ethylhexanol (Reaction 1, (3)), 2-ethyl-hexanol upon heating and acid catalysis converts to 2-octenes and 3-octenes, some of the chemicals that were observed in the chromatograms.



Reaction 2. A route for decomposition of 1,2-benzenedicarboxylic acid, di(2-ethylhexyl) ester to 1,2-benzenedicarboxylic acid, mono(2-ethylhexyl) ester, 2-ethylhexanol, 2-octene, and 3-octene.

Sample 15 was the last sample collected before the air-condenser was clogged with precipitations of the solids. Further studies showed these solids are mostly derivatives of phthalic and benzoic acids (see identification of solids). The content of the main peak at 1.34 min (Fig 8 Sample 15) is HCl and moisture (Fig 13). The TIC at 1.48 contains also moisture and HCl plus other chemicals, when the background is subtracted from the TIC, 2-methyl-butane a C_5 saturated hydrocarbon was identified. At 1.608 min 2,3-dimethylbutane C_6H_{14} , from 1.7-2.27 min a mixture of hexanes was viable. The high abundant materials at 2.408 min identified as benzene, C_6H_6 . At 4.292 min toluene, and at 5.058 - 5.84 min 2-ethyl-1-hexene C_8H_{16} , at 5.850 min 3-dimethyl-1-hexene C_8H_{16} were identified. At 8.058 min ethyl-benzene C_8H_{10} , at 8.433 p-xylene C_8H_{10} , at 9.30 min m-xylene C_8H_{10} , at 11.417 min cumene C_9H_{12} , at 11.467 min to 11.617 min 4-chloro-2,4-dimethylhexane $C_8H_{17}Cl$. At 12.108 min benzonitrile C_7H_5N , at 12.208 min hemimellitene, 1,2,3-trimethyl benzene, C_9H_{12} , at 12.275 min undecane, $C_{11}H_{24}$ at 12.617 min 3,3-diethylpentane $C_{10}H_{22}$. It is hard to analyze after RT15 min because of super saturation of the column. Table 10 shows the detailed list of the 50 major compounds in this sample.

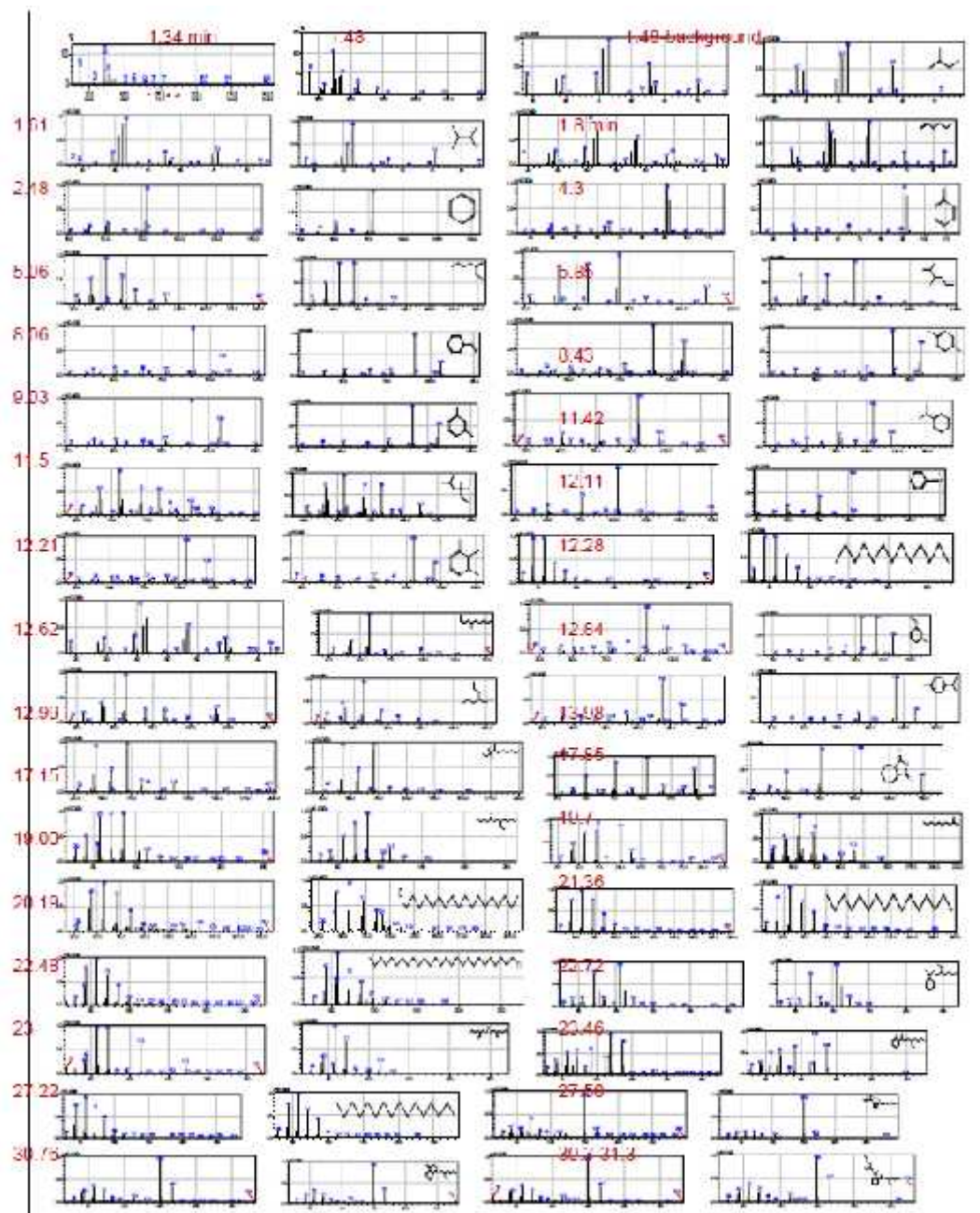


Fig13. Mass spectrum of some picks of sample 15 (identified with their retention time (min)) and the most similar MS from NIST library

Table 10. 50 major chemicals identified in the liquid obtained by the pyrolysis of LEG sample 15

Retention Time	Start Time	End Time	Area %	Name
1.451	1.108	1.592	0.60	HCl

1.616	1.592	1.650	0.09	Butane, 2,3-dimethyl-
1.773	1.650	1.800	0.25	Pentane, 2,3-dimethyl-
1.823	1.800	2.158	0.47	Cyclopropane, 1,2,3-trimethyl-
2.192	2.158	2.233	0.05	Cyclopentene, 1-methyl-
2.416	2.233	2.742	2.92	Benzene
2.812	2.742	3.092	0.56	Oxalic acid, allyl nonyl ester
3.131	3.092	3.317	0.19	Cyclopentane, 1-ethyl-2-methyl-
3.342	3.317	3.425	0.05	Cyclopentane, ethyl-
3.484	3.425	3.633	0.09	Cyclohexene, 4-methyl-
3.990	3.633	4.025	0.33	Cyclopentane, 2-isopropyl-1,3-dimethyl-
4.301	4.025	4.792	3.61	Toluene
5.452	4.792	5.742	5.82	3-Heptene, 3-methyl-
5.857	5.742	6.242	2.13	2,3-Dimethyl-1-hexene
6.341	6.242	6.492	0.21	1,3-Dimethyl-1-cyclohexene
6.542	6.492	6.767	0.16	Heptane, 2,6-dimethyl-
6.932	6.767	7.317	0.22	Dichloroacetic acid, 2-ethylcyclohexyl ester
8.070	7.317	8.192	0.91	Ethylbenzene
8.442	8.192	8.942	1.74	p-Xylene
9.306	8.942	9.992	2.28	Benzene, 1,3-dimethyl-
10.294	9.992	11.042	1.40	cis-1,4-Dimethyl-2-methylenecyclohexane
11.478	11.042	11.742	3.67	Acetophenone
12.113	11.742	12.492	3.69	Benzonitrile
12.627	12.492	12.742	1.50	Pentane, 3,3-diethyl-
13.098	12.742	13.642	5.56	2-Propyl-1-pentanol
13.794	13.642	13.892	1.49	Benzhydrazide, N2-(2-methoxy-5-nitrobenzylideno)-
13.993	13.892	14.592	4.10	1,4-Cyclohexadiene, 3-ethenyl-1,2-dimethyl-
14.688	14.592	14.942	1.64	Benzene, 1,2,3,5-tetramethyl-
15.289	14.942	15.692	4.49	2,4-Dimethylstyrene
16.055	15.692	16.392	4.72	Naphthalene, 1,2,3,4-tetrahydro-1-methyl-
17.537	16.392	17.742	9.75	Benzoic acid
17.980	17.742	18.242	3.42	Phthalic anhydride
18.946	18.242	19.342	7.27	Tetradecane
19.545	19.342	19.792	2.90	2-Oxabicyclo[2.2.1]heptan-3-one-1-carboxylic acid, 4,7,7-trimethyl-, 8-oxo-8a-methyldecalin-1-yl ester
19.841	19.792	19.942	0.93	Naphthalene, 2,3-dimethyl-
20.046	19.942	21.092	6.58	1H-Isoindole-1,3(2H)-dione, N-ethyl-
21.237	21.092	22.242	4.86	5-(4-Methylphenyl)cyclohexane-1,3-dione
22.300	22.242	22.592	1.21	Undecyl heptafluorobutyrate
22.728	22.592	23.142	1.68	Benzoic acid, 2-ethylhexyl ester
23.522	23.142	24.942	3.17	Hexadecane
24.992	24.942	27.042	1.46	2H-1-Benzopyran-3-ol, 3,4-dihydro-5,7-dimethoxy-2-(3,4,5-trimethoxyphenyl)-, (2R-cis)-
27.472	27.042	28.042	0.54	Phthalic acid, decyl 2-ethylhexyl ester
28.192	28.042	28.942	0.21	1,2-Benzenedicarboxylic acid, diisooctyl ester
29.042	28.942	29.142	0.04	Dimethyl 1,2-diisopropenyltricyclo[3.1.0.0(2,4)]hexane-3,6-dicarboxylate
29.338	29.142	29.442	0.06	1,1-Diphenyl-2-propanol

29.533	29.442	30.042	0.12	Indan-2-one, 1-[2-chlorobenzylidene]-
30.764	30.042	31.842	0.86	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester

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Sample E

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Sample E was selected for GC-MS analysis as a representative sample of fourth stage of pyrolysis.

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The aqueous samples A to C were strongly acidic. However, TIC of sample E did not show any presence of HCl. The highest abundance chemicals are: at 1.29 min allyl vinyl ether, at 2.18 min 1-pentene, at 2.5 min benzene, at 4.7 min toluene, 5 min octene, 7.9-9.4 xylene isomers, 9.6 min 2,4-dimethylhexane, 11.34 min ethyltoluene, 11.87 min benzonitrile, 12.08 min hemimellitene, 12.26 min undecane, 17.72 min, 1,2,4-trimethyl-benzene, at 12.94 min 2-ethyl-1-hexanol, at 13.86 min 1-ethyl-2,3-dimethyl-benzene, at 13.99 2-ethyl-1,4-dimethyl-benzene, at 14.08 4-dodecene, at 14.24 tridecane, 14.95 ethyl-styrene, at 15.17 min o-allyl-toluene, 15.25 min 2-methylindene, 15.84 naphthalene 15.79 min 1,3-dimethylindan 15.9 1-Isopropylvinyl)benzene. Table 11 shows the 50 major chemicals in the sample E.

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3.3. THE SOLID SAMPLES

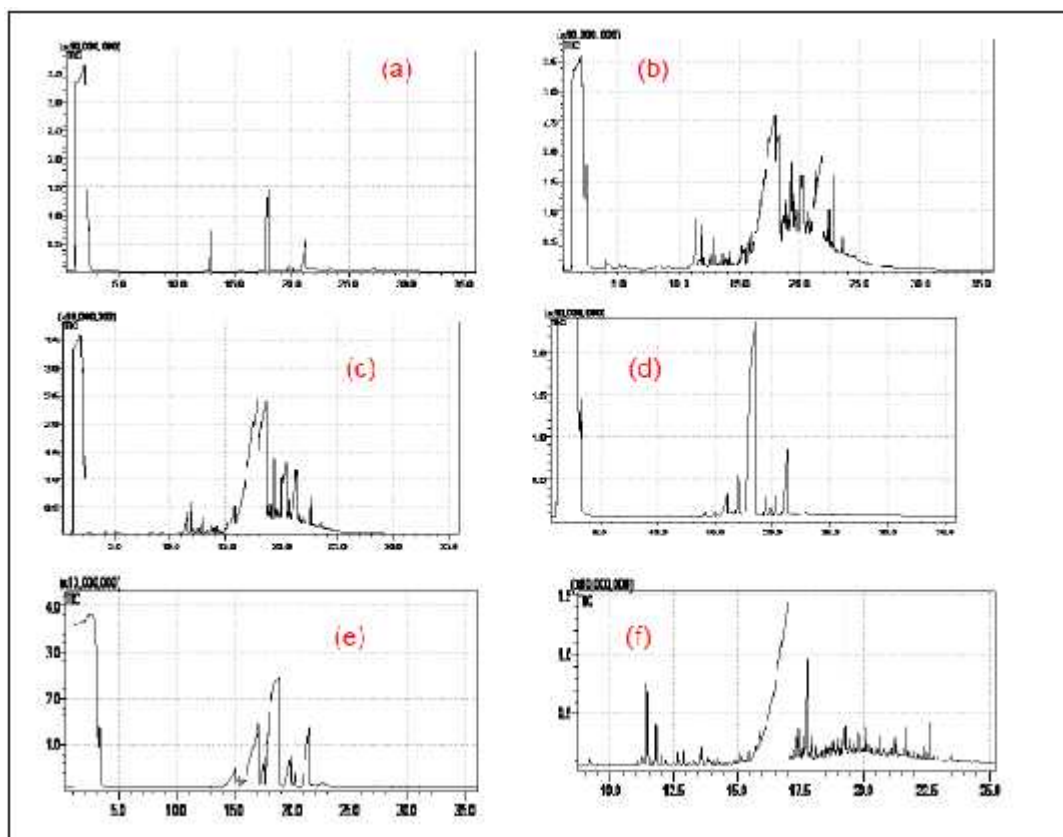
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The yellow solid sample (Fig 2c) and a sample of the precipitants in the condenser were dissolved in methanol water (90:10) for GC-MS analysis. Fig 14 contains the TIC of the both sample.



529

Fig 14. TIC of methanol soluble solids: (a) Solids crystallized out of joint (Fig 2c), (b) Hexanes soluble parts of the solid from inside of condenser (Fig 4g), (c) Crude solid precipitated in condenser, (d) Purified crystals (Fig 16e), (e) The solid precipitated in water (Fig 16 a), (f) hexanes soluble (Fig 16 c), and its expansion (9-25 min).

3.3.1. Yellow Sample Crystallized Outside of the Joints.

The yellow solid sample resulted from the leak out of the distillates from the distillation head joints, crystallized outside of receiver joints (Fig 2c) was soluble in methanol and boiling water. The aqueous solution was acidic. The sample was recrystallized in water (Fig 16c). The GC-MS of a few crude crystals dissolved in methanol (Fig 14a) showed three main picks identified as 2-ethyl-hexanol, phthalic anhydride or phthalic acid, and the final peak was di-(1-hexen-5-yl) ester $C_{20}H_{26}O_4$ as identified in Fig 15.

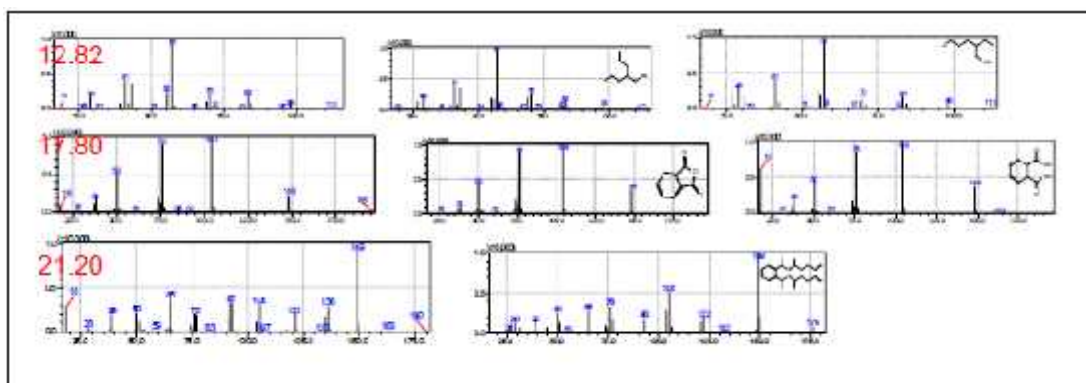
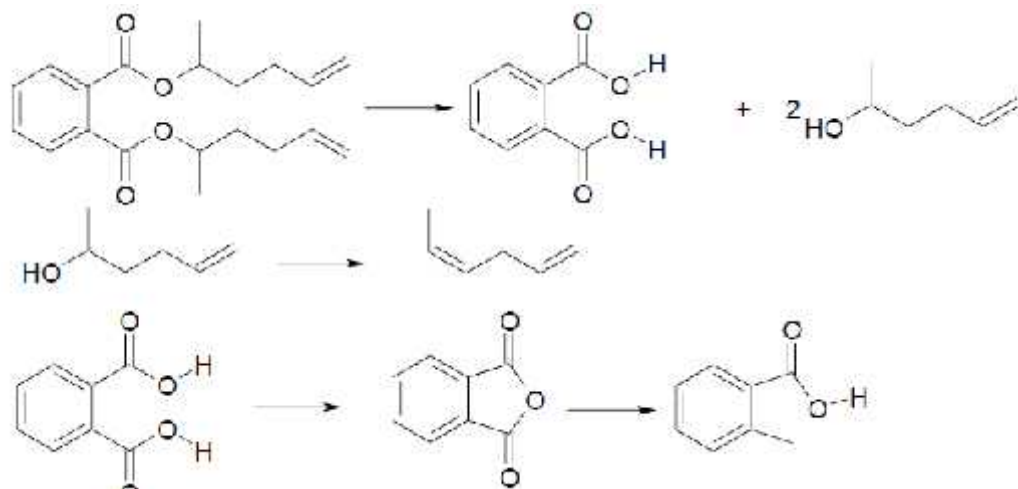


Fig 15. Mass spectrum of some picks of water-soluble solid (identified with their retention time (min)) and the most similar MS from NIST library for comparison.

The result of GC-MS (Fig 15) indicates that the crystal was di-(1-hexen-5-yl) ester of phthalic acid. The ester is stable, however, it partially decomposed in GC chamber at high temperature (250°C) to alcohol, and acid; the acid is not stable over 210°C temperature then it converts to anhydride. Also, the alcohols by losing water converted to alkenes (Reaction 3).



Reaction 3. A schematic degradation of di-(1-hexen-5-yl) phthalate to phthalic anhydride and alcohol, then the alcohol to di-ene.

3.3.2. The solid sample within the distillation head.

The solid deposited in the distillation head during the pyrolysis reaction was contaminated with the distillates liquids. This sample in the boiling water was separated into two phases; water soluble and water insoluble materials (Fig 16a). The same sample in hexanes also was separated into two phases; part of this sample was hexanes soluble, red in color (Fig 16b); and most of solid was insoluble in hexanes then precipitated (pale color solids). Both solutions were strongly acidic. After water solution cooled down, amorphous and crystalline materials were visible in the aqueous layer and organic materials on top layer (Fig 16c). Both solutions were strongly acidic. After water solution cooled down, amorphous and crystalline materials were visible in the aqueous layer and organic materials on top layer (Fig 16c).

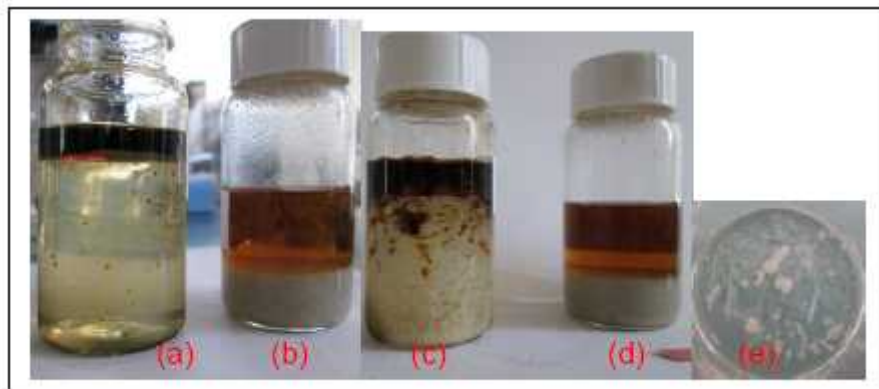
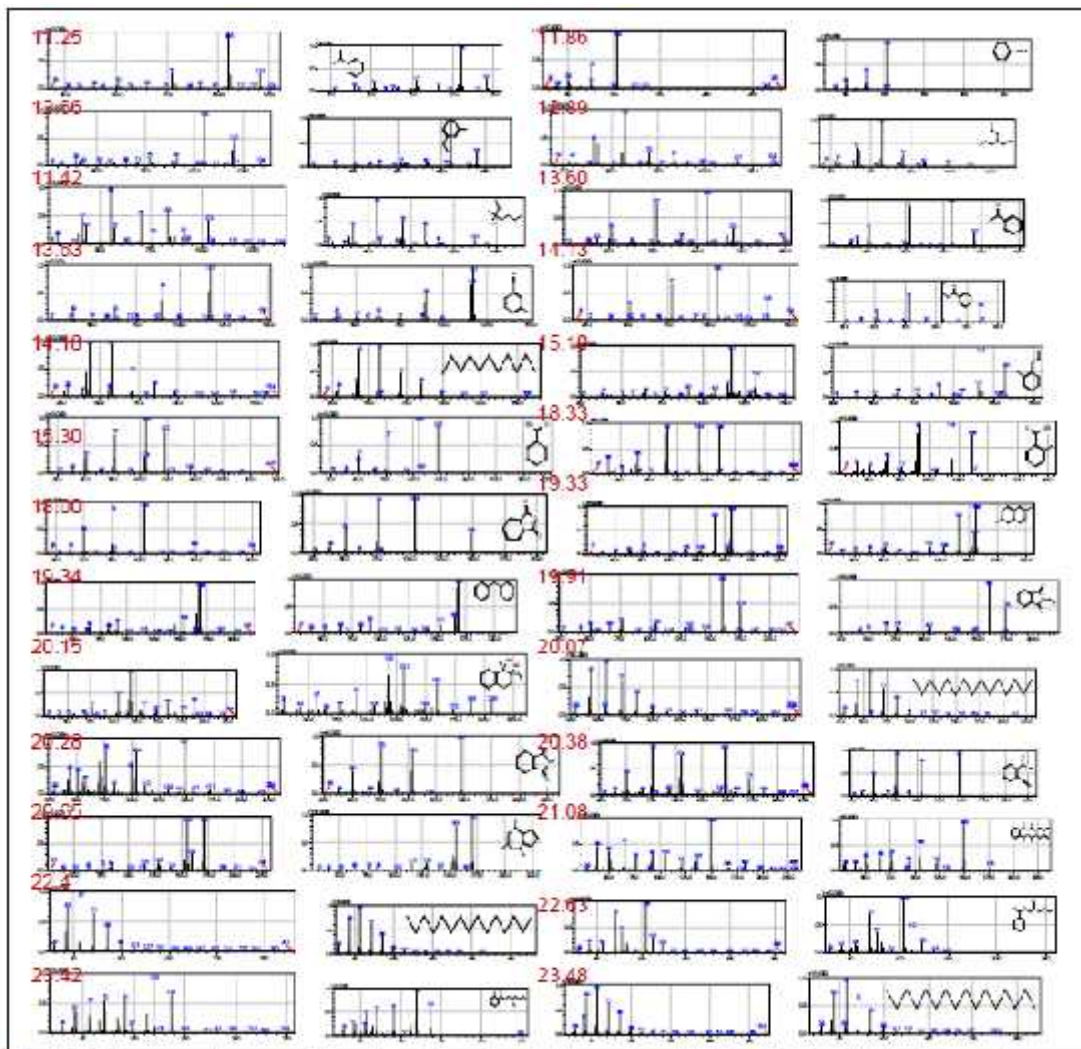


Fig 16. Solubility of solid products: (a) in hot water, (b) in hexanes, (c) precipitation and crystallization of the solids in water (d) no change in hexanes solution (e) shape of pure crystals in water.

3.3.3. The Crude Solids at Third Distillation

The TIC of crude solid precipitate in the condenser dissolved in methanol/water mixture (90:10) showed several chemicals. As Fig 16a and b showed, these solid are contaminated with liquid distillates. The first wide and high peak in TIC relates to solvent, methanol and water mixture (90/10), the end shoulder at 2.283 min was hydrogen chloride. The first major

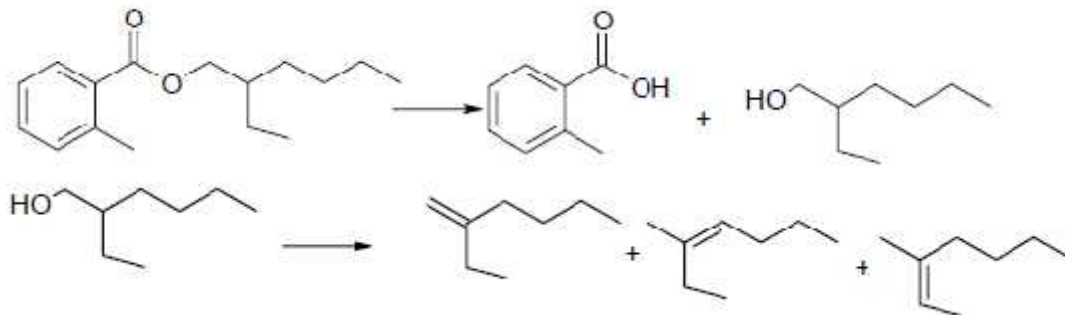
577 peak (11.250 min) was cumene or Isopropylbenzene C_9H_{12} , and the one at (11.417 min) was
 578 3-chloro-3-methylheptane, $C_8H_{17}Cl$, or $C_{11}H_{22}$. The sharp peak at 11.858 min was
 579 benzonitrile C_7H_5N , and the next small one (12.658 min) was 1-methyl-3-ethylbenzene
 580 C_9H_{12} , and the next to it (12.892 min) was 2-propyl-1-pentanol $C_8H_{18}O$. Fig 17 shows the
 581 MS of the major compound in the sample and the most similar compound to it searched from
 582 NIST library.
 583



584
 585 Fig 17. MS scan of the major compound of methanol soluble crud solid (identified with their
 586 retention time (min)) and the most similar MS from NIST library for comparisons.
 587

588 The major compound of this chromatogram is located between 15-24 min. At 15.300 min
 589 benzoic acid $C_7H_6O_2$, at 17.033 min 2-methylbenzoic acid $C_8H_8O_2$, at 18.100 min to 18.583
 590 min phthalic anhydride $C_8H_4O_3$, at 19.317 min 2,6-dimethylnaphthalene $C_{12}H_{12}$, at 19.375
 591 min diphenyl methane at 19.908 min N-ethylphthalimide $C_{10}H_9NO_2$, at 20.283 min
 592 phthalimide or phthalimidomethyl 3-methoxybenzoate, $C_{17}H_{13}NO_5$, (20.375 min to 20.433
 593 min) o-cyanobenzoic acid, $C_8H_5NO_2$, at 21.075 min to 21.433 min phthalic acid, di-(1-hexen-

594 5-yl) ester $C_{20}H_{26}O_4$, at 22.633 min ethylhexylbenzoate $C_{15}H_{22}O_2$, at 23.417 min o-toluic acid,
 595 2-ethylhexyl ester $C_{16}H_{24}O_2$, were identified
 596



597
 598 Reaction 4. A schematic degradation of 2-ethylhexyl-2-methylbenzoate to 2-methylbenzoic
 599 acid and 2-ethylhexanol, then the alcohol to alkene.
 600

601 3.3.4. The Clear Crystals

602 A portion of the solid precipitated in water was dissolved in boiling water then recrystallized
 603 in water (Fig 16e). The TIC of these crystals dissolved in methanol/water mixture (Fig 14d)
 604 showed three compounds at RT of 13.04, 14.17-17.1, 17.5-18.4, 19.2-21.3 min, identified as
 605 2-ethyl-hexanol, benzoic acid (96% similarity), phthalic anhydride (96% similarity), phthalic
 606 acid, di(1-hexen-5-yl)ester (similarity 82%). The assumption that these crystals could be
 607 di(1-hexene 5-yl)phthalate that under high temperature in GC injector decomposed to the
 608 indicated compounds is also a valid assumption (Reaction 2).
 609

610 3.3.5. The Precipitated in Water

611 The TIC of amorphous sample precipitated in water (Fig 14e) is very similar to the purified
 612 crystals (3.3.4). MS shows the following chemicals: Benzoic acid (15.1 -17.1 min), 2-methyl
 613 benzoic acid (17.59 min), phthalic anhydride (17.69-19.93 min), 3-formyl-benzoic acid
 614 (19.40-19.81 min), phthalimide (19.93 min), phthalic acid, di-(1-hexen-5-yl) ester (20.80-
 615 21.50).

616 The results indicated that the amorphous material is a mixture composed of phthalic acid,
 617 benzoic acid their derivatives.
 618

619 3.3.6. The Hexane Soluble

620 The TIC of hexane soluble portion of the precipitates in the condensers (Fig 14a) showed
 621 chemical content similar to the liquid fractions in addition to be saturated with slightly soluble
 622 components which were detected in section 3.3.5. The following are a list of the major
 623 chemicals in sample: 3-chloro-3-methylheptane (11.87 min), benzonitrile (12.03 min),
 624 benzoic acid (15.50-17.0), phthalic acid (17.74), dimethylnaphthalene (18.74), di-(1-hexen-5-
 625 yl) ester of phthalic acid (21.65), ethylhexyl benzoate (22.62). Table 11 contains a more
 626 extended list of the chemicals which were attached to the solids precipitated in the
 627 condenser.
 628

629 Table 11. Major chemicals in attached to the solid precipitated in the condenser.

RT (min)	Start	End	% Area	Name
4.928	4.875	5.042	0.02	Cyclopentane, 1-ethyl-3-methyl-, cis-
5.224	5.042	5.342	0.06	3-Octene, (Z)-

5.476	5.342	5.533	0.02	2-Octene, (E)-
5.585	5.533	5.683	0.01	1,6-Heptadiene, 2,3,6-trimethyl-
7.929	7.867	8.058	0.03	Ethylbenzene
8.274	8.200	8.408	0.09	o-Xylene
8.450	8.408	8.542	0.01	Octane, 3-methyl-
9.138	9.083	9.333	0.08	o-Xylene
9.489	9.425	9.575	0.02	Nonane
11.000	10.967	11.042	0.01	Benzene, propyl-
11.080	11.042	11.150	0.04	1-Pentanol, 4-methyl-2-propyl-
11.253	11.150	11.358	0.15	Benzene, 1-ethyl-3-methyl-
11.408	11.358	11.567	0.55	Heptane, 3-chloro-3-methyl-
11.668	11.567	11.708	0.02	Benzene, 1-ethyl-3-methyl-
11.781	11.708	11.883	0.29	Benzonitrile
11.925	11.883	11.958	0.01	Carbonic acid, phenyl undec-10-enyl ester
11.993	11.958	12.092	0.08	Benzene, 1,3,5-trimethyl-
12.183	12.092	12.283	0.04	Octane, 2,7-dimethyl-
12.453	12.283	12.492	0.05	Pentane, 3,3-diethyl-
12.517	12.492	12.567	0.01	Cyclopropane, 1,2-dimethyl-3-pentyl-
12.642	12.567	12.775	0.11	Benzene, 1,2,3-trimethyl-
12.860	12.775	12.975	0.13	2-Propyl-1-pentanol
13.017	12.975	13.067	0.01	2-Tridecen-1-ol, (E)-
13.100	13.067	13.167	0.02	Indene
13.262	13.167	13.300	0.03	Benzene, 1-methyl-3-propyl-
13.353	13.300	13.383	0.03	1,2,3,4,5,8-Hexahydronaphthalene
13.408	13.383	13.442	0.02	Benzene, 4-ethyl-1,2-dimethyl-
13.467	13.442	13.500	0.01	3a,6-Methano-3aH-indene, 2,3,4,5,6,7-hexahydro-
13.593	13.500	13.675	0.14	Benzeneacetonitrile, .alpha.-acetyl-
13.806	13.675	13.892	0.08	Benzene, 1-ethyl-2,3-dimethyl-
13.928	13.892	13.983	0.04	1,3-Cyclopentadiene, 1,2,3,4-tetramethyl-5-methylene-
14.039	13.983	14.092	0.04	5-Chloropentanoic acid, 2-octyl ester
14.191	14.092	14.242	0.05	Undecane
14.318	14.242	14.350	0.03	Benzene, 4-ethyl-1,2-dimethyl-
14.375	14.350	14.408	0.01	Benzene, 1-methyl-4-(1-methylpropyl)-
14.494	14.408	14.525	0.01	Spiro[3.5]nona-5,7-dien-1-one, 5,9,9-trimethyl-
14.572	14.525	14.625	0.02	Benzene, 1,2,4,5-tetramethyl-
14.676	14.642	14.708	0.01	Decane, 3,7-dimethyl-
14.905	14.833	14.950	0.03	1H-Indene, 2,3-dihydro-5-methyl-
14.990	14.950	15.025	0.02	Benzene, 1,4-diethyl-2-methyl-
15.095	15.025	15.158	0.10	1-Phenyl-1-butene
15.183	15.158	15.242	0.05	2-Methylindene
15.300	15.242	15.325	0.03	Benzene, 2,4-diethyl-1-methyl-
15.350	15.325	15.417	0.04	1-Butanone, 1-phenyl-
15.447	15.417	15.475	0.06	Benzoic acid, ethyl ester
15.729	15.475	15.775	0.42	1H-Indene, 2,3-dihydro-1,6-dimethyl-
15.900	15.775	15.950	0.58	1H-Indene, 2,3-dihydro-1,6-dimethyl-
17.046	15.950	17.142	14.49	Benzoic acid
17.215	17.142	17.250	0.12	1H-Indene, 2,3-dihydro-1,3-dimethyl-
17.412	17.250	17.475	0.49	Naphthalene, 2-methyl-
17.516	17.475	17.550	0.10	Benzene, 4-(2-butenyl)-1,2-dimethyl-, (E)-
17.597	17.550	17.633	0.12	1H-Inden-1-one, 2,3-dihydro-2-methyl-
17.795	17.633	17.817	1.27	Phthalic anhydride

17.891	17.817	17.942	0.21	1H-Indene, 2,3-dihydro-1,1,5-trimethyl-
17.958	17.942	18.008	0.04	3-(4-Cyanomethyl-1H-pyrrol-3-yl)-propionitrile
18.033	18.008	18.083	0.06	3-Hydroxymethyl-4-(1-hydroxy-2-methylprop-2-enyl)toluene
18.133	18.083	18.183	0.15	Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl-
18.211	18.183	18.258	0.09	1(3H)-Isobenzofuranone
18.308	18.258	18.342	0.11	Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-
18.415	18.342	18.492	0.20	2-Buten-1-one, 2-methyl-1-phenyl-
18.542	18.492	18.567	0.13	Benzene, 2-(2-butenyl)-1,3,5-trimethyl-
18.605	18.567	18.683	0.21	Biphenyl
18.759	18.683	18.783	0.21	Silane, trichlorooctadecyl-
18.817	18.783	18.842	0.13	Naphthalene, 2-ethyl-
18.870	18.842	18.917	0.13	Naphthalene, 1-ethyl-
18.969	18.917	19.050	0.26	Naphthalene, 2,6-dimethyl-
19.090	19.050	19.133	0.13	7-Isopropylidenebicyclo[2.2.1]hept-5-en-2-one p-toluenesulfonylhydrazone
19.229	19.133	19.258	0.67	Naphthalene, 2,6-dimethyl-
19.314	19.258	19.400	0.31	Diphenylmethane
19.445	19.400	19.583	0.39	Benzene, 2-chloro-1,3,5-trimethyl-
19.637	19.583	19.667	0.16	Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-
19.755	19.667	19.792	0.29	o-Cyanobenzoic acid
19.855	19.792	19.883	0.27	1H-Isoindole-1,3(2H)-dione, N-ethyl-
19.958	19.883	19.983	0.17	Hexadecane, 1,16-dichloro-
20.050	19.983	20.083	0.25	Pentadecane
20.107	20.083	20.192	0.22	1,2-Naphthalenediol, 2-ethyl-1,2,3,4-tetrahydro-1-methyl-, cis-
20.245	20.192	20.358	0.31	Hexanoic acid, 2-ethylhexyl ester
20.383	20.358	20.417	0.08	11-Dodecen-1-ol, 2,4,6-trimethyl-, (R,R,R)-
20.490	20.417	20.550	0.20	Naphthalene, 1,4,6-trimethyl-
20.600	20.550	20.650	0.21	Azulene, 4,6,8-trimethyl-
20.667	20.650	20.683	0.04	Benzenebutanoic acid, 2,5-dimethyl-
20.700	20.683	20.750	0.08	Benzyl alcohol, .alpha.-isobutyl-2,4,5-trimethyl-
20.798	20.750	20.900	0.21	3-(2-Methyl-propenyl)-1H-indene
20.983	20.900	20.992	0.10	Benzene, 1,1'-[3-(3-cyclopentylpropyl)-1,5-pentanediy]bis-
21.011	20.992	21.067	0.10	Azulene, 4,6,8-trimethyl-
21.108	21.067	21.133	0.10	2,3,4-Trifluorobenzoic acid, 3-phenylpropyl ester
21.167	21.133	21.192	0.07	Cycloeicosane
21.257	21.192	21.283	0.17	Pentadecane
21.317	21.283	21.367	0.13	3-(2-Methyl-propenyl)-1H-indene
21.417	21.367	21.525	0.15	1,1'-Biphenyl, 2,4'-dimethyl-
21.680	21.525	21.717	0.48	Phthalic acid, di-(1-hexen-5-yl) ester
21.776	21.717	21.808	0.10	.gamma.-Chlorobutyrophenone
21.825	21.808	21.875	0.05	Heptacosane, 1-chloro-
21.926	21.875	21.975	0.07	Naphthalene, 1-methyl-7-(1-methylethyl)-
22.005	21.975	22.092	0.11	Benzene, 1,1'-(1,3-propanediyl)bis-
22.183	22.092	22.208	0.07	N-n-Butylphthalimide
22.245	22.208	22.292	0.05	7-Heptadecene, 1-chloro-
22.320	22.292	22.375	0.05	Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-
22.400	22.375	22.433	0.07	Hexadecane
22.500	22.433	22.558	0.05	Hexane, 2-phenyl-3-propyl-
22.616	22.558	22.658	0.17	Benzoic acid, 2-ethylhexyl ester
22.692	22.658	22.733	0.03	1,1'-Biphenyl, 2,4'-dimethyl-

22.772	22.733	22.833	0.05	1,2-Diphenyl-1-isocyanoethane
22.915	22.833	22.958	0.04	1,2-Diphenylcyclopropane
22.992	22.958	23.050	0.02	Azulene, 7-ethyl-1,4-dimethyl-
23.150	23.050	23.192	0.01	Benzene, 1,1'-(1-methyl-1,3-propanediyl)bis-
23.413	23.375	23.458	0.02	o-Toluic acid, 2-ethylhexyl ester
23.486	23.458	23.592	0.03	Pentadecane
23.824	23.792	23.900	0.01	Benzene, 1,1'-(1,3-butadienyldiene)bis-

4. CONCLUSION AND REMARKS

The results showed part of the pyrolysis products of LSGs are reached in many varieties of chlorinated compounds which are potentially hazardous for environment and human health. Comparing TICs (Fig 8) showed that by increasing pyrolysis time the relative amount of HCl and water in the samples decreased. This is consistent with the reported mechanism for thermal degradation of chlorinated polymers and alcohols. The amount of benzene produced is increasing by time well visible in the sample 15, the peak height and area of benzene is higher than combined HCl and moisture. All samples had three kinds of materials, volatile organic hydrocarbons that is suitable as gasoline, visible in the chromatogram from 1.58 to 10 min mainly C₆ to C₁₁ hydrocarbons; semi-volatile materials are visible after 11 min with carbons numbers higher than 12, and solid organic acids and esters that appears after 18 min such as phthalic acids and benzoic acid and their esters used as plasticizers in the processing of the LSG.

The liquid produced from pyrolysis of LEGs is saturated with hydrochloric acid, phthalic acid, benzoic acid and their derivatives. Before using it as clean fuel particularly fuel for internal combustion engines, further refinements -- separating fuel worthy chemicals from acids and chlorinated compounds -- is required. The compositions of the remaining materials at the end of the process also depended on the heating limit of the reactor. Below 500°C the residues contains carbon compounds, however above 800°C the residue is carbon free. Therefore, the nature, yields, and the chemical compositions of the liquids produced by pyrolysis of the waste gloves depend on the engineering of the process and the heating limitation of the reactor. The last but not the least, the products of pyrolysis contained highly reactive chemicals; these materials are not chemically stable making the storage life of these liquids rather short. Therefore, the products must be stabilized either by chemical stabilizers or hydrogenation for long time storage promptly after collection.

In this experiment, 23% of the materials remained in bottom of the reactor as hard dark solid residue, 36% was collected as liquid saturated in solids, and 4% of the total mass was collected as solid deposited in the condenser. Therefore, 36% of the mass was converted to HCl, and carbon derivatives, C, C₂, C₃, C₄, and C₅ gases. Neoprene has 40% by mass chlorine, and potentially, 41.2% of it will convert to HCl, a theoretical yield of 58.8% was expected for combined carbon derivative gases, liquid and solid products from pure neoprene pyrolysis. The higher yield of combined solids and liquids (63%) is due to production of some chlorinated hydrocarbons; in addition to this a part of gloves mass is chlorine-free fillers and plasticizers.

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673 **COMPETING INTERESTS**

674 Authors have declared that no competing interests exist.

675

676 **REFERENCES**

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680 reproduction in any medium, provided the original work is properly cited.

1. Halla, W.J., Zakariab, N., and Williams, P.T. (2009) Pyrolysis of latex gloves in the presence of y-zeolite. *Waste Management*, 29 (2), 797-803.
- 2 Behzadi, S. & Farid, M. (2006) Feedstock Recycling and Pyrolysis of Waste Plastics: Converting Waste Plastics into Diesel and Other Fuels Edited by J. Scheirs and W. Kaminsky, John Wiley & Sons, Ltd ISBN: 0-470-02152-7 P531.
3. Rajan, V.V., Dierkes, W.K., Joseph, R. and Noordermeer, J.W.M., (2006) Science and technology of rubber reclamation with special attention to NR-based waste latex products. *Progress in Polymer Science* 31, 811-834
- 4 Ahmad, D. Dr. S. (2011) Malaysia will be global center of excellence for rubber. *Rubber Asia* 25(5) 34-41.
http://rubberasia.com/v2/index.php?option=com_content&view=article&id=558&catid=3 downloaded July 11, 2013. <http://www.deepdyve.com/lp/elsevier/pyrolysis-of-latex-gloves-in-the-presence-of-y-zeolite-dbmp0uWTza>
5. "Medical Gloves and Gowns". FDA. Retrieved 2010-03-10.
- 6 http://en.wikipedia.org/wiki/Medical_glove Retrieved 2013-6-5.
- 7 "Glove manufacturing". Ansell.eu. Retrieved 2012-12-14
- 8 Werner Obrecht, Jean-Pierre Lambert, Michael Happ, Christiane Oppenheimer-Stix, John Dunn and Ralf Krüger "Rubber, 4. Emulsion Rubbers" in Ullmann's Encyclopedia of Industrial Chemistry, 2012, Wiley-VCH, Weinheim.doi:10.1002/14356007.o23_o01
- 9 Furman E. Glenn. "Chloroprene Polymers". *Encyclopedia of Polymer Science and Technology*. doi:10.1002/0471440264.pst053
- 10 Lehmann, F.A. & Brauer, G.M. (1961). Analysis of pyrolyzates of polystyrene and poly(methyl methacrylate) by gas chromatography. *Analytical Chemistry* 33(6) 679-676.
- 11 Gargallo, L., Hamidi, N., Radic, D., & Tagles, L.H. (1989). Thermogravimetric Analysis of Poly(dialkylphenyl methacrylate)s, *Thermochimica Acta*, 143, 75-84.
- 12 Gumula, T, Paluszkiwicz, C., & Blazewicz, S. (2009).Study on Thermal Decomposition Processes of Polysiloxane Polymers—From polymer to Nanosized Silicon Carbide. *Journal of Analytical and Applied Pyrolysis*, 86(2), 375–380.
- 13 Insura, N., Onwudili, J.A. & Williams, P.T. (2010). Catalytic Pyrolysis of Low-Density Polyethylene over Alumina-Supported Noble Metal Catalysts. *Energy & Fuels*, 24(8), 4231-4240.
- 14 Faravelli, T., Bozzano, G., Colombo, M., Ranzi, E., & Dente, M. (2003). Kinetic modeling of the thermal degradation of polyethylene and polystyrene mixtures. *Journal of Analytical and Applied Pyrolysis*, 70(2) 761 – 777.
- 15 Koo, J.K., Kim, S.W., & Waste. (1993). Reaction Kinetic Model for Optimal Pyrolysis of Plastic Waste Mixtures. *Management & Research* 11(6) 515-529.
- 16 Costa, P., Pinto, F., Ramos, A. M., Gulyurtlu, I., Cabrita, I., & Bernardo, M. S. (2010). Study of the Pyrolysis Kinetics of a Mixture of Polyethylene, Polypropylene, and Polystyrene. *Energy & Fuels*. 24(12), 6239-6247.
- 17 Smolders, K., & Baeyens, J. (2004). Thermal Degradation of PMMA in Fluidized Beds. *Waste Management*, 24(8), 849-857.

- 18 Straus, S & Madorsky, S. L. (1953). Pyrolysis of Styrene, Acrylate, and Isoprene Polymers in a Vacuum. *Journal of Research of the National Bureau of Standards*, 50(3), 2405.
- 19 Cooley, J. H. & Williams, R. V. (2003). The Pyrolysis of Polystyrene. *Chem. Educator*, 8, 309-311.
- 20 Onwudili, J.A., Insura, N., & Williams, P.T.(2009). Composition of products from the pyrolysis of polyethylene and polystyrene in a closed batch reactor: Effects of temperature and residence time. *Journal of Analytical and Applied Pyrolysis*, 86(2), 293-303.
- 21 Koo, J.K., Kim, S.W., & Seo, Y.H. (1991). Characterization of aromatic hydrocarbon formation from pyrolysis of polyethylene-polystyrene mixtures. *Resources, Conservation & Recycling*, 5(4), 365-382.
- 22 Huggett, C. & Levin, B.C. (1987) Toxicity of the Pyrolysis and Combustion Products of Poly (Vinyl Chlorides): A Literature Assessment. *Fire and Materials*, VOL. II, 131-142.
- 23 Miranda, R., Pakdel, H., Roy, C., & Vasile, C. (2001). Vacuum pyrolysis of commingled plastics containing PVC II. Product analysis. *Polymer Degradation and Stability*. 73(1), 47-67.
- 24 Lee, K.H. (2011). Pyrolysis of waste polystyrene and High-Density Polyethylene. Korea Institute of Energy Research. South Korea.
- 25 Li Chuantong, Liu Rong and Tang Bo, 2004. Study on Kinetic Properties of Pyrolysis for Hospital Solid Wastes, Proceedings, 3rd ICIPEC, Hangzhou, China, October.
- 26 Achilias, D.S., Roupakias, C., Megalokonomos, P., Lappas, A.A., & Antonakou, E.V. (2007). Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP), *Journal of Hazardous Materials*, 149(3), 536-542
- 27 Mastellone, M.L., & Arena, U. (2004). Bed Defluidisation during the Fluidised Bed Pyrolysis of Plastic Waste Mixtures. *Polymer Degradation and Stability*, 85(3), 1051-1058.
- 28 Zakaria, N., Ani F. N., Yunus, M.N.M., and Husain, M.A.S. (2011) Oxidative pyrolysis of examination rubber gloves in the integral pyrolysis test plant, *International Journal of Mechanical and Materials Engineering (IJMME)*, Vol.6, No.1, 1-9
- 29 Environmental Protection Agency (EPA), (2010). Cycling: Frequent Questions. Retrieved July 2012, from <http://www.epa.gov/epawaste/conservation/materials/ecycling/faq.htm> and; <http://www.epa.gov/epawaste/conservation/materials/plastics.htm>
- 30 Zhu H. M., Yan J. H., Jiang X. G., Lai Y. E., Cen K. F. 2008. Study on pyrolysis of typical medical waste materials by using TG-FTIR analysis, *Journal of Hazardous Materials*, 153, 670-676.
- 31 Sarker, M. Rashid, M.M. Rahman, R. & Molla, (2012). M. Conversion of Low Density Polyethylene (LDPE) and Polypropylene (PP) waste plastics into liquid fuel using thermal cracking process. *British Journal of Environment & Climate Change*, 2(1): 1-11.
- 32 Williams, E.A., & Williams, P.T. (1997). Analysis of products derived from the fast pyrolysis of plastic waste. *Journal of Analytical and Applied Pyrolysis*, 40-41, 347-363.
- 33 Williams, P.T., & Williams, E.A. (1999). Fluidised Bed Pyrolysis of Low Density Polyethylene to Produce Petrochemical Feedstock. *Journal of Analytical and Applied Pyrolysis*, 51(1), 107 – 126.
- 34 Lee, K.-H.(2009). Thermal Degradation of Heavy Pyrolytic Oil in a Batch and Continuous Reaction System. *Journal of Analytical and Applied Pyrolysis*, 86(2), 348–353.
- 35 Kaminsky, W., Predel, M., & Sadiki, A. (2004). Feedstock Recycling of Polymers by Pyrolysis in a Fluidised Bed. *Polymer Degradation and Stability*, 85(3), 1045-1050.
- 36 Schmidt, H. & Kaminsky, W. (2001). Pyrolysis of Oil Sludge in a Fluidised Bed Reactor. *Chemosphere* 45(3), 285-290.
- 37 For examples look at Envion (<http://www.envion.com>) or Agilyx (<http://green.blogs.nytimes.com/tag/diesel/>) or Polymer Energy® (<http://www.polymerenergy.com/technology>)
- 38 4R Sustainability, Inc., (2011). Conversion Technology: A Complement to Plastic Recycling, Portland, OR 97203
- 39 Pinto F., Costa P., Gulyurtlu I., & Cabrita I. (1999). Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield, *Journal of Analytical and Applied Pyrolysis*, 51(1), 39-55.

-
- 40 Bushnell, K. (2012). Plastic Bags: What About Recycling Them? The Sierra Club. Retrieved June 2010 from http://www.sierraclub.org/sustainable_consumption/articles/bags2.asp.
 - 41 Brebu, M., Ucar, S., Vasile, C., & Yanik, J. (2010). Co-pyrolysis of Pine Cone with Synthetic Polymers. *Fuel*, 89(8), 1911-1918.
 - 42 Buah, W.K., Cunliffe, A.M., & Williams, P.T. (2007). Characterization of Products from the Pyrolysis of Municipal Solid Waste. *Process Safety and Environmental Protection*, 85(5), 450-457.
 - 43 Caglar, A. & Aydinli, A. (2009). Isothermal Co-pyrolysis of Hazelnut Shell and Ultra-high Molecular Weight Polyethylene: The Effect of Temperature and Composition on the Amount of Pyrolysis Products. *Journal of Analytical and Applied Pyrolysis*, 86(2), 304–309.
 - 44 On-Line <http://www.chemspider.com/Chemical-Structure.13619.html> Downloaded July 9 2013.