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

Nasrollah Hamidi[1*], Ruhullah Massoudi[1], Sujan Shrestha[2,3], Lycinda Lalmansingh[2,3], Travis Pascoe[1,2], Comfort Oriakhi[1,2], and Louis Whitesides[4]

[1]Department of Biological and Physical Sciences, South Carolina State University, Orangeburg, SC 29117.
[2]Undergraduate Student
[3]Department of Civil and Mechanical Engineering and Technology, South Carolina State University, Orangeburg, SC 29117
[4]1890–Research, South Carolina State University, Orangeburg, SC 29117.

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; and assisted with the revision of the manuscript. Author SS participated in performing the experiments, collecting 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, and 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 stages. All authors read and approved the final manuscript.

ABSTRACT

Aims: The aim of this investigation was to develop a methodology that provides insights to clean up environmental pollution caused by the ever increasing amount of waste plastic materials. 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 research 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 such 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 LSGs into useful liquid and solid chemicals. The LSGs were pushed into the reactor one by one without cutting. Prior to pyrolysis, the thermal stability of materials were determined by

thermogravimetric analysis (from 50ºC to 800ºC) with a heating rate of 10ºC/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 it depended on the nature of constituent polymers. The highest decomposition rates were observed at temperatures around 410ºC. 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 LSG 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 plastics, followed with eight member carbon isomers, and 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, the liquids were 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, phthalic acid derivatives.

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 spectrometer, MS: mass spectrometer, WHO: world health organization,

1. INTRODUCTION

Recycling plastics waste by thermal cracking or pyrolysis is one of the most used methods [e.g. 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 chains of hydrocarbons and polymers into shorter chain molecules. The waste laboratory safety gloves (LSGs) in this process decomposed randomly into three phases of matter: gaseous materials such as HCl and C1 to C4 hydrocarbons, a complex mixture of liquid, and solids. By pyrolysis, the solid wastes were converted to liquids with potentialities of transportation fuel and the chemical energies stored within LSGs waste were recycled. Also, this process provided environmental advantage by minimizing plastic pollution [1,2].

The sources of waste pollution originating with LSGs are safety precautions in professional work. The safety protection required in scientific laboratories, technological industries, and health industries has an increased demand for the production of latex gloves. As a consequence, the demand for natural rubber latex has risen about four times from 159 thousand tons in 1984 to 597 thousand tons in 2003 [1,3]. Since then in 2005, Malaysia, one of the world's leading rubber glove manufacturers, alone consumed 226.2 thousand tons of natural rubber for glove production [3]. Additionally, the production of natural rubber is expected to increase worldwide. Reports from Indonesia and Malaysia show effort to

increase their output to 2900 thousand tons and 970 thousand tons, respectively. The private sector in Vietnam is also expected to increase their natural demand to 780 thousand tons, while Cambodia has announced that they expect an increase in their plantation area (45 thousand tons) [4].

Examination gloves or disposable gloves also are used during medical examinations and procedures and as safety protection in work to prevent contaminations [5,6]. They are available in the 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 better precision and sensitivity and are made to a higher standard than examination gloves. The gloves that are used in chemistry laboratories as safety protection media are examination gloves (Fig 1a). The wastes LEGs, reported here, were generated in our laboratory as safety protection ware.

Examination gloves are made of diverse polymers including latex, nitrile rubber, vinyl and neoprene. Neoprene or polychloroprene $(-CH_2-CCl=CH-CH_2-)_n$ is a family of synthetic rubbers that are produced by free-radical polymerization of 2-chlorobutadiene ($CH_2=CCl-CH=CH_2$)[8]. It 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' interest from both points of view: stability of goods produced [10,11], and reeducation of generated wastes [e.g. 12,13,14]. Thus, decomposition kinetics of polymeric materials [e.g.15,16] and the mechanism of decomposition have been studied by many researchers [e.g.17,18]. Researchers have discovered that some widely used polymeric materials such as poly(methyl methacrylate) (PMMA), upon heating, decomposed to original monomers [19] likewise polystyrene (PS) to styrene [20,21,22,23] with very high yields at micro-scales. Thus, a relatively inexpensive source to the basic chemicals for manufacturing industries was considered. However, the most-used polymeric materials such as poly(vinyl chloride) (PVC), decomposed to smaller stable toxic corrosive chemical that were part of the original constituents mer of the polymers. For example, PVC, upon heating, first decomposed to hydrogen chloride and unsaturated polymers; these newly produced unsaturated polymers upon heating decomposed later to other chemicals [eg 24,25,26]. Pyrolysis process of neoprene is very similar to that of PVC. It first produces HCl [27] and unsaturated polymers. 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 whenever we deal with waste processing and recovery which is the subject of this work.

The pyrolysis of LSGs got relevance since it is not as easy as recycling of styrene based materials. Especial design requirements of this process have attracted the attention of engineers for designing pilot plants [28] at the kg level. On the other hand, the wide use of LSGs resulted in the accumulation 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, and 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 chemicals produced from pyrolysis of LSGs. More research and relevant data are required for better

understanding of the process [28]. A study on kinetic properties of pyrolysis of selected medicals wastes such as absorbent cotton, medical respirator, bamboo sticks [30] and cotton gauges, packaging boxes, capsule plates and transfusion tubes [25] were conducted by a number of researchers [e.g.25, 30].

To describe a current picture of the situation, it is safe to say, wastes of modern materials are accumulated without effective decomposition and recycling routes in the landfills. The increase of petroleum and petrochemical prices opened the way 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 [e.g. 29-33]. Literature abounds on the recycling of these non-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 [e.g. 39]. However, run-away plastic wastes are continuing to be an enormous hazard on the surface and surface water such as waterways, seas and oceans, endangering safe life for both animals and humans [40].

A real waste container in the waste collection site contains many kinds of waste. Therefore, co-pyrolysis of waste plastic with other natural wastes is relevant for researchers. 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 LSGs which are neoprene based material. LSGs are disposed regularly, in teaching and research laboratories, and in hospitals and medical offices, as mentioned above. Therefore, the conversion of LSGs to useful chemicals has both economic and environmental benefits. Thus, the material used here were waste LSGs (not freshly prepared polymers, or clean products supplied by manufacturers) to simulate real conditions at collection centers and the results were close to those expected from waste processing pyrolysis.

2. MATERIALS, INSTRUMENTATION, AND METHODS

2.1 Materials

The material used (Fig 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 50ºC to 800ºC with a heating rate of 10ºC/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 40ºC, followed by a 10ºC/min temperature increase to 220ºC 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 weighing 879.8 g (Fig 1b) were placed into the reactor (Fig 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. Table 1 shows the stages of heating and decomposition process of LEGs. At 253°C vapors resulting from decomposing LEGs filled up the flask, air condenser, and the other flasks (Fig 1d). The first drop of condensate (97°C) was collected into the recipient graduated funnel when the melt temperature reached 488ºC. The drops at the time of condensation were clear liquid but when they reached to the bottom of the container the color was changed from bright yellow to dark green. As time passed the color of the liquid became darker.

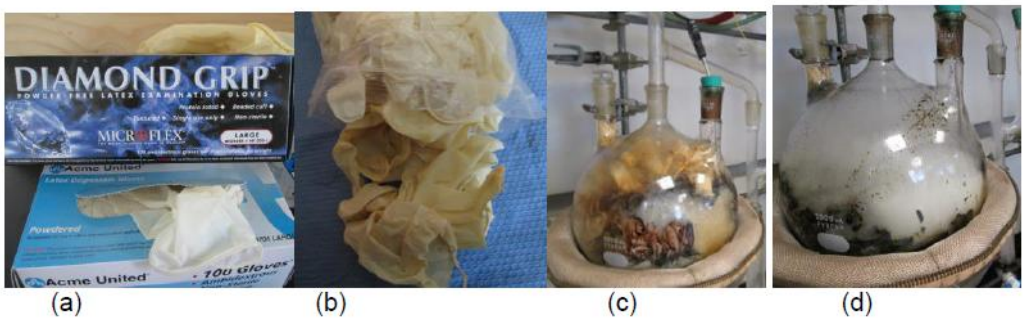


Fig 1. Step-by-step illustration of decomposition process of LEGs: (a) LEGs before use; (b) waste LEGs collected during one year (2012); (c) LEGs loaded in the reactor; (d) the reactor at 393°C.

Table 1. The thermal history of the reactor: first attempt to pyrolysis of LEGs.

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

At this moment, the pressure of gases opened the joints, the liquids and uncondensed vapors were leaking out from the joints of the Claisen adaptor; therefore, the reaction was stopped. Days later, 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 a mixture of methanol:water (90:10 V:V) and boiling water. The aqueous solution of the solid was strongly acidic. The pyrolysis was resumed after the joints were cleaned (Fig 2d). Table 2 summarizes the results of the second attempt to pyrolysis LEGs.

Fig 2. Step-by-step illustration of the decomposition process of LEGs: (a) the white needle shaped crystals grown in tope of the cold residues; (b) accumulation of solids out of the joints; (c) a sample of the solids; (d) the setup; (e) the condenser with solids.

Table 2. Thermal history of the reactor: second attempt to pyrolysis LEGs.

Time	Temperature (°C)			Comments
	T 1	T 2	T 3	
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.

The reaction was stopped since unusually high vapor pressure opened the joints and the solids were deposited again inside the path of condenser (Fig 2e) and outsides of the joints.

Continuation of Reaction (third time)

The collection parts of the system were cleaned and dried prior to resuming the pyrolysis. The pyrolysis lasted ~ 5 hours. Pyrolysis was discontinued when the cloud of vapors was solidified around the neck of the reaction vessel. Table 3 (appendix) shows the steps of the pyrolysis.

At the beginning the thermometer (T1, T2, and T3) readings were 23.0°C, as was the room temperature. After six minutes of heating, a dark steam filled the flask then the argon gas valve was turned on (T1's reading was at 25.6°C; this indicated that the thermistor was not touching the bottom of the flask). After a period of 14 minutes the temperature of T1 increased to 89° C, while T2's temperature was recorded at 51° C. During this period, clouds of vapor travelled through the air-condenser and the first drops of liquid appeared around the road of the steam in the air condenser. Simultaneously, solid depositions in the air-condenser nearly blocked it; however, the incoming distillate dissolved most of the solids and moved them into samples (Fig 3a to d). Next, a greenish solid filled the condenser but most of it was washed away by distillates (Fig 3e). After that, a reddish solid filled the path then it was washed away by incoming distillates (Fig 3f). At the end a dark yellow solid remained in the condenser and the path of liquid.

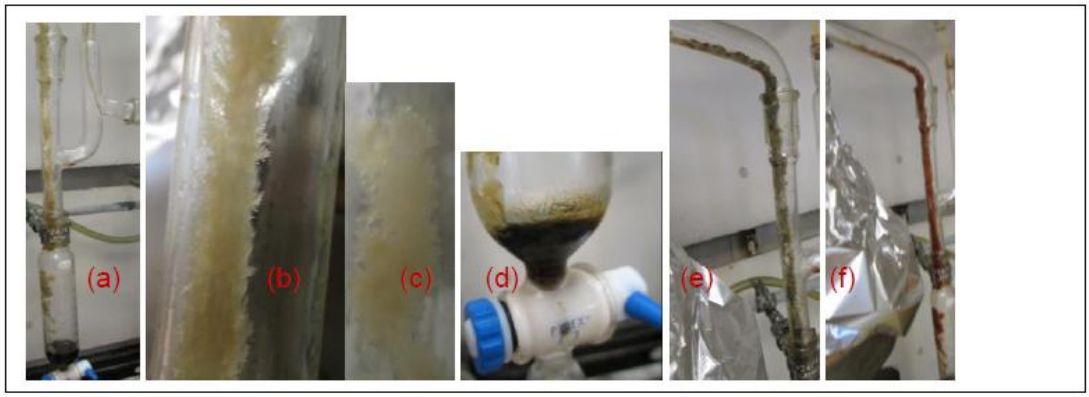


Fig 3. Step-by-step illustration of the decomposition process of LEGs (a) solids deposited in the condenser; (b) and (c) magnification of selected sections of (a); (d) crystallization of solids in the collection funnel; (e) deposit of greenish solids; (f) deposit of reddish solids.

After a period of fifteen minutes the first drop of liquid was observed in the funnel (Fig 4b), and T2 readings were constant, recorded 51° C. The initial sample collected was clear yellow in color and part of the liquid was solidified around the glass funnel. After a few hours, the collected liquid divided into three phases, organic, aqueous, and solid crystals (Fig 4d and e).

As soon as a sample was collected, it was taken for GC-MS analysis. If GC-MS was busy in the previous sample, and then the sample 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 3 (appendix) shows the time and amount of sample collected. Noticeable changes in the color of the solids were observed: changed from almond (fig 4a-4d) to a darkish green (Fig 4e).

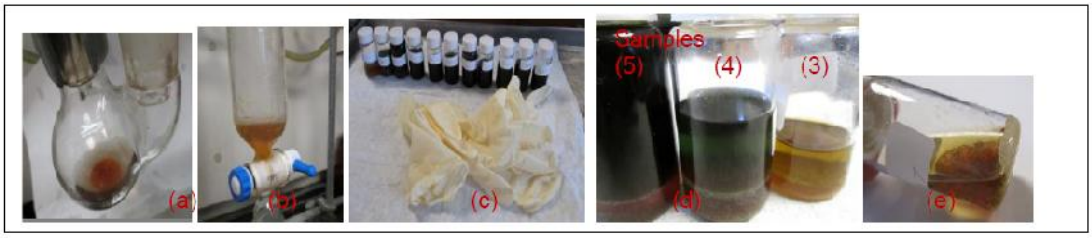


Fig 4. Results of pyrolysis of LEGs: (a) liquid condensed in the second flask; (b) The apparent of the first sample collected in the graduated funnel; (c) eleven samples collected from pyrolysis of LEGs; (d) magnification of the appearance of samples 3, 4 and 5; (e) sample 1 after 3 hours; it divided 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 that it had two phases: aqueous and organic. Later on, when we examined the samples again, it was composed of three phase of organic, aqueous, and solid (Fig 4e).

The Extraction with Boiling Water.

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

Continuation of the Pyrolysis.

The condensers and receivers were washed well with methanol/water, 90/10, (v:v) then reassembled. The heater was set on 6 (scale of 1 to 10). After recovering 50 mL of water (with a few mL of organic layers on top of it (sample A, not shown here) the receiver for Sample B was placed under the funnel. Six more samples were collected (Fig 5 B-G). The sample B showed an aqueous phase with crystals suspended in it and an organic phase on top. The amount of organic phase increased in time as the water contents of the reaction flask consumed (Fig 5 B and C). By advancing the pyrolysis, the amount of organic layer increased and its color become darker. The last samples (Fig 5 samples F and G) had no-water and its color was dark-red (Fig 5 samples E to G).

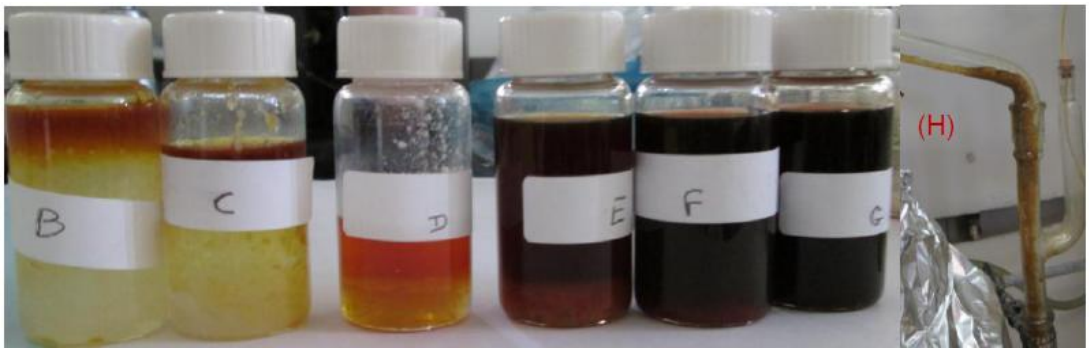


Fig 5. The samples collected after aqueous extractions and addition of 100 mL of water to the reaction flask.

During sample E collection, the condenser was filled with reddish solids (Fig 5H). Most of these solids were dissolved in the distillates during the collection of samples E to G. At the end of pyrolysis at T1 = 620°C, little solids remained in the condenser.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric Analysis

About 12 mg of a LEG was cut into small pieces that could fit into the TGA pan (Fig 6a). The initial attempt was a heating scan from 50°C to 600°C under nitrogen. The end product was a grey color and contained dark chunks (Fig 6b) which was indicative of incomplete decomposition. The next heating ramp was from 50°C to 800°C (under nitrogen), which resulted in white solid end products (Fig 6c). This solid was soluble in water; the pH of its solution was very basic (Fig 6d).

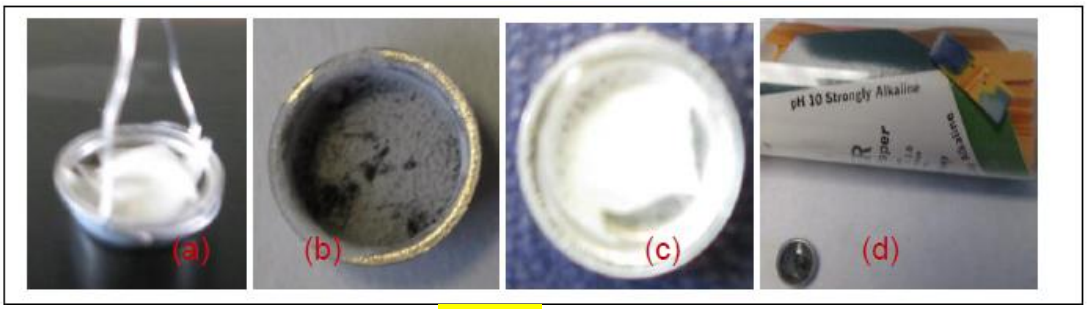


Fig 6. Thermogravimetric analysis of LEGs: (a) pan loaded with 12 mg of LEG; (b) the remains after heated to 600°C; (c) the ashes at 800°C; (d) strongly alkaline pH of the aqueous solution of the ashes.

Figure 7 shows the results of thermogravimetric studies of LEGs, both powdered and un-powdered. The thermal stability of both types of LEGs are very similar; the decomposition began around 350°C reaching the highest rate at 410°C. The decomposition reaction was complete at 500°C; the residues of powdered LEG (~30%) were much more than that of powder-free sample LEG (~12%) as was expected. A second stage of decomposition was observed around 625°C for powder free LEG and 650° for powdered LEG. The resulting ashes were white in color (Fig 6c), and soluble in water, producing a strongly basic solution (Fig 6d) which is a property of active metal oxides. The thermogravimetric data agreed with the observations in the reactor (Tables 1 to 4).

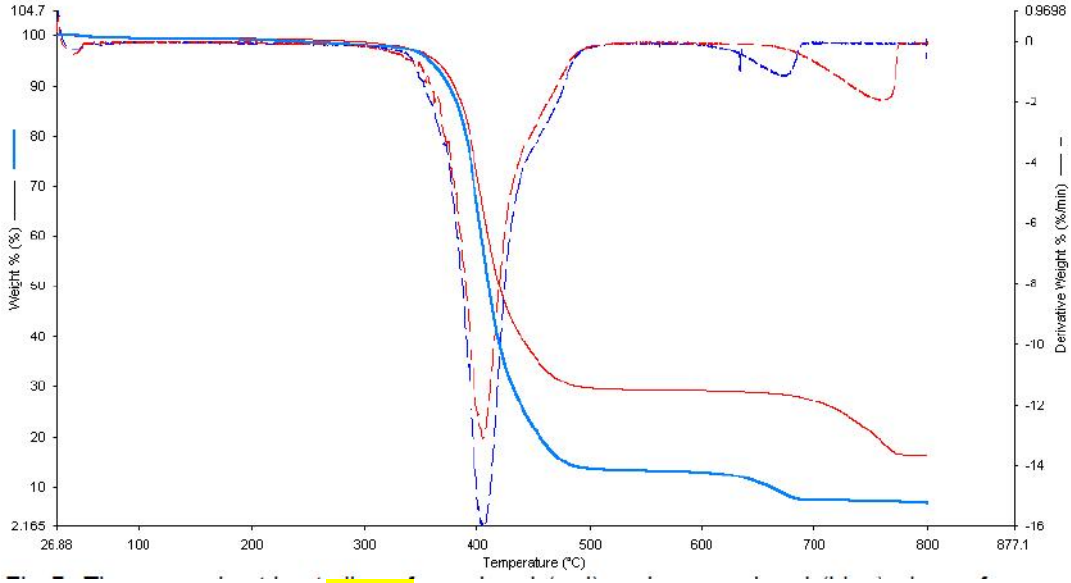


Fig 7. Thermogravimetric results of powdered (red line) and un-powdered (blue line) gloves from 50°C of 800°C under 10 mL/min N_2 (g) with heating rate of 10°C/min.

3.2 Analysis of Liquid Samples Obtained from Pyrolysis of LEGs

The pyrolysis of the LEGs resulted in 25 samples. All samples were analyzed by GC-MS. Most of the chromatograms were similar to each other; however, nine of them were slightly different (Fig 8). Below, these nine TICs will be annualized.

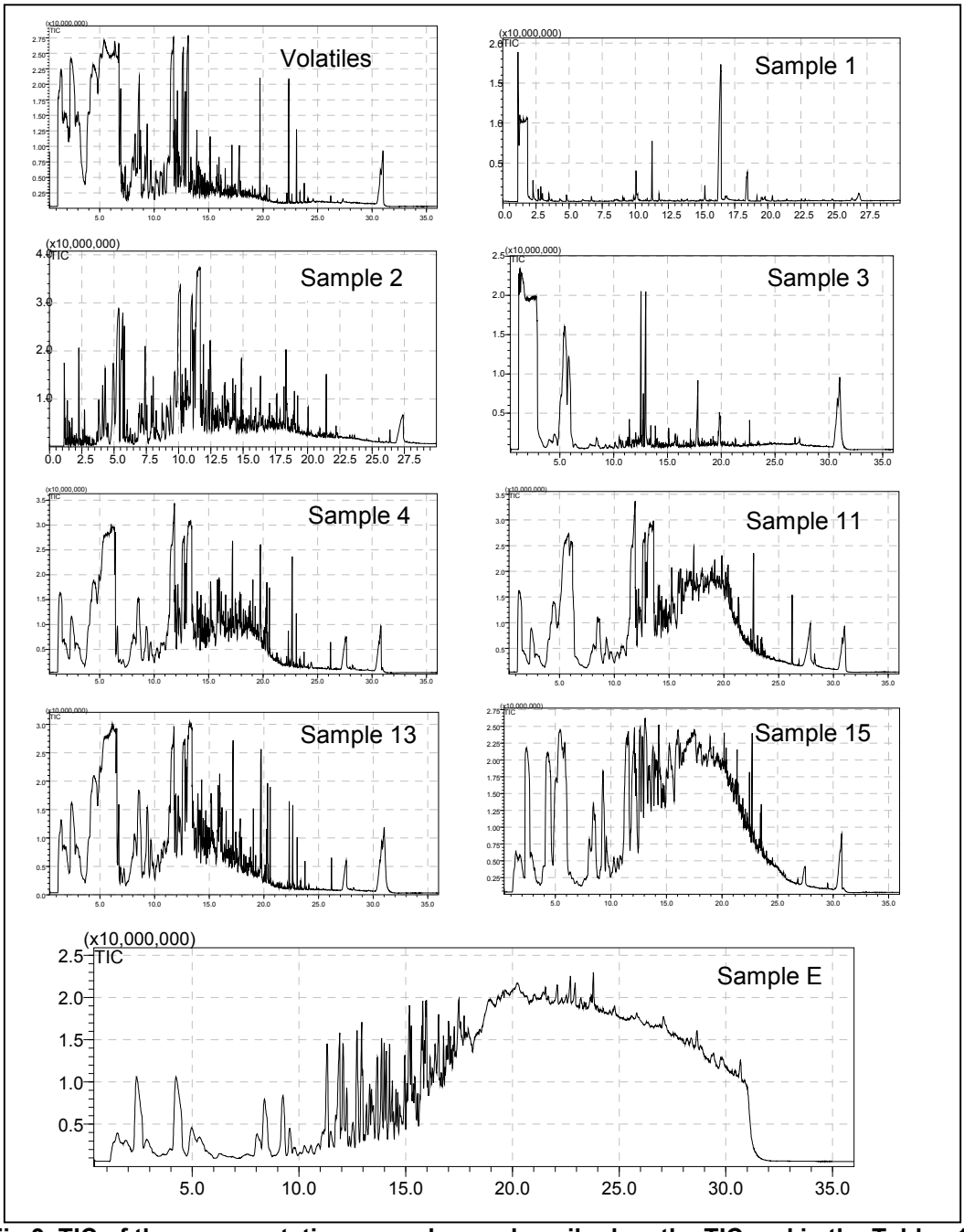


Fig 9. TIC of the representatives samples as described on the TIC and in the Tables 1, 3, and 4

3.2.1. The most volatile sample

The most volatile sample consisted of the chemical that escaped the first collection container and accumulated in the second container (Fig 4a) equipped with a water condenser, was kept cold in an ice-water bath. As the TIC (Fig 8 Volatiles) showed, the first peak at the chromatogram (1.15-1.36 min) was hydrogen chloride as expected; the next peak (1.36-1.56) represents a mixture of HCl and C_5 compounds, C_5H_{10}, then, at the end of the peak (1.58-2.27 min) various isomers of C_6 compounds, C_6H_{12}, both cyclic and acyclic, with one saturated element, the broad peak located at 2.27-2.74min was benzene, C_6H_6, at 2.78-4.30 min C_7 compounds were visible such as 2,2-dimethylpentane (2.742 min) then heptene isomers (2.78-3.59 min), octene isomers appeared at 3.68 – 6.79 min while toluene, C_7H_8, was co-eluted with octenes (4.11-4.81 min). Then C_8 compounds with two unsaturated units were at 6.82-7.48 min. From 7.48 – 9.00 min the dimethyl benzene derivatives (C_8) with C_9 linear isomers were visible. The peak at 11.45-11.83 was hard to identify; the NIST [44] library identifies it as 3-chlor-3-ethyl heptane with 88% similarity, however, the M/z = 91 may be indicative of a benezylic 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, identified as various isomers of straight chains $C_{11}H_{22}$ (192°C), $C_{11}H_{20}$ (bp 196°C), and $C_{11}H_{24}$ (bp 196°C) [45]. Table 5 (in the appendix) provides the list of major chemicals identified from the most volatile sample. Also, a comparison between the mass-spectrum (MS) of the compounds in the sample of volatiles and the MS in the NIST library is available (Fig 9 Appendix).

3.2.2. Sample 1

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

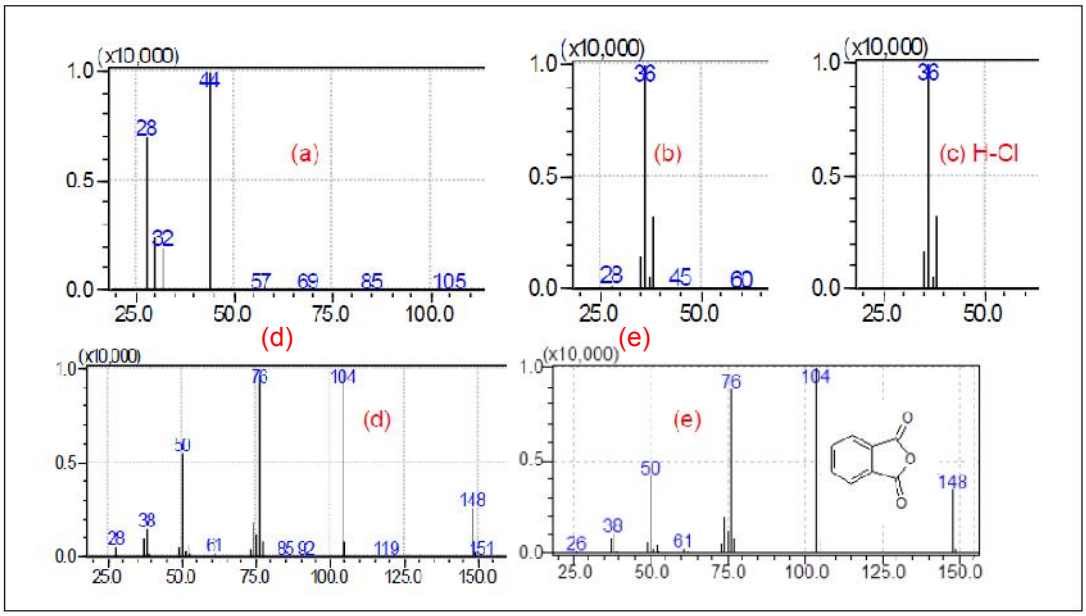
As the TIC of sample 1 (Fig 8 sample 1) showed there were over 170 chemicals identified by the auto-research of GC-MS with very low concentration relative to HCl. Fig 10a shows the background or the baseline of the chromatogram at the initial time, these M/z are the ion of gasses that were dissolved in the sample: CO_2, (M/z = 44 Da), oxygen (M/z = 32 Da), NO (M/z = 30 Da), and N_2 (M/z = 28 Da). These low molar mass compounds produced from decomposition of gloves; dissolved in the sample, as was also 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 10b) which has been identified as HCl, hydrogen chloride (Fig 10c). 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 reached in oxygenated compounds. The pH of sample 1 was below 2 measured by a pH-paper which confirmed strong acidity of the sample. HCl produced by decomposition of chlorinated polymers that were 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 then to 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, phthatic anhydride (Fig 10 d) which appeared at 16.4 min

(compared with NIST library (Fig 10e)), and at 18.5 min; phthalimide also appeared besides saturated and unsaturated hydrocarbons (Table 6 appendix).

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 of products such as benzene and its derivatives, and other polycyclic compounds such as naphthalene and its derivatives as reported by other researchers [27]. 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 reached to the end of condenser, the color changed, and within the liquid, solid crystals appeared. Table 6 (in appendix) shows 50 major chemicals identified by the NIST library in sample 1.

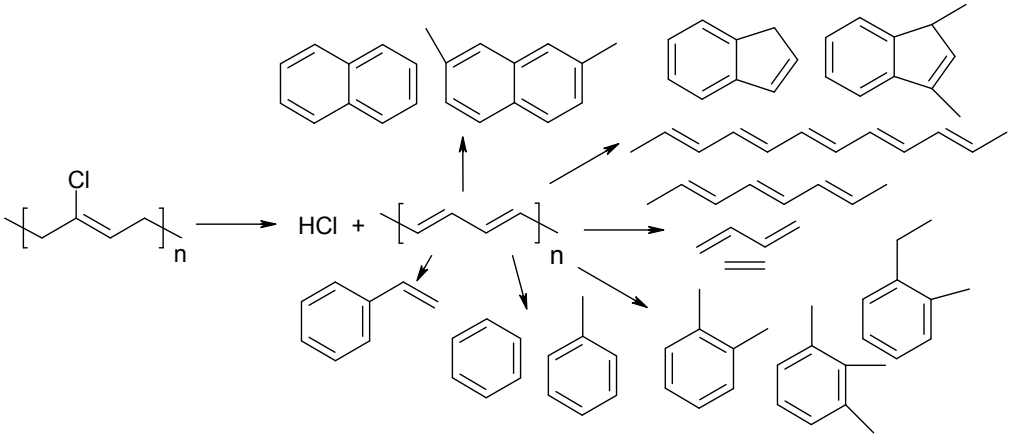


g 10. (a) A background scan at the beginning of TIC; (b) a scan from the peak appeared from 1.25 -1.75 min; (c) MS of HCl from NIST library; (d) a scan of compound appeared at 16.45 min; (e) a MS of phthalic anhydride from the NIST library.

3.2.3. Sample 2

Table 7 (appendix) shows 50 major chemicals identified from sample 2. This sample contained 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 [25]. Then these unsaturated polymers decompose to other hydrocarbons (Reaction 1). Therefore, most of HCl were volatilized and left the reactor prior and during the collection of first the sample. The major chemicals of sample 2 were: at 2.27 min (Fig 11a) identified as benzene (Fig 11b). From 4.75 min to 5.89 min the isomers of octane were identified: at 5.27 min 3-ethyl-2-hexene at 5.65 min 3-methyl-2-heptene and at 5.79 min 2-octene. The next major chemical at 7.40 min is another isomer of C_8, xylene. At 8.25 min nonane was identified. At 8.70 min the C_{10} isomers began to appear. Also, some chlorinated compounds were 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 (Fig 11c) was a chlorinated compound, 1-chloro-2-ethyl-heptane (Fig 11d), and at 11.49 min

(Fig 11e) 2-ethyl-hexanol either (Fig 11f) or 6-methyl-3-undecene was identified. At 11.90 min it was also a C_{10} isomer which was identified as 3-carene. The reaction below (Reaction 1) shows a possible decomposition and composition path for the chemicals produced from pyrolysis of neoprene and detected by GC-MS.



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

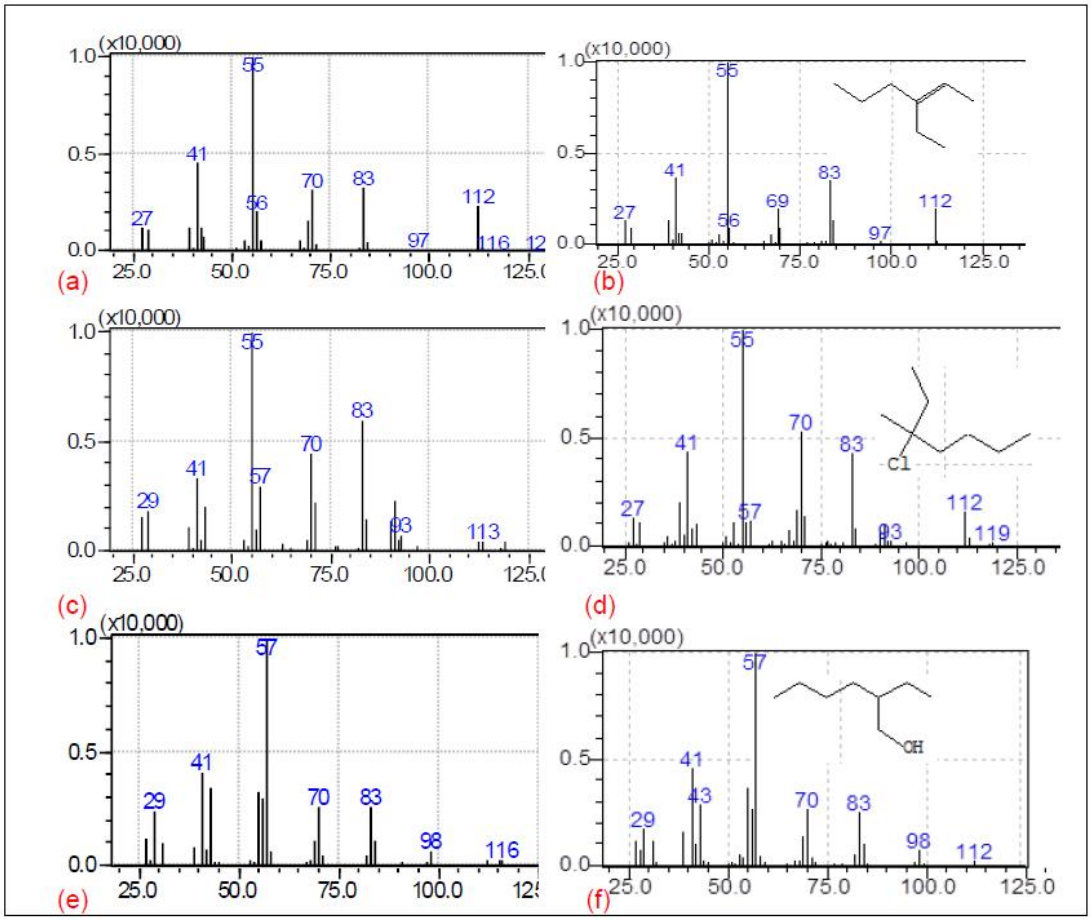


Fig 11. MS of the major compounds in sample 2 compared with the MS of the most similar compound from NIST library.

3.2.4. Sample 3

This sample was the first to be collected during the third attempt to pyrolyze LEGs. Table 8 shows 50 of the major chemicals in sample 3. Chromatogram of sample 3 (Fig 8 Sample 3) shows nine major compounds, though the total number of chemicals in the sample exceed 250. The background at the initial time (Fig 12 a) shows moisture (M/z = 18 in excess), nitrogen (M/z = 28), oxygen (M/z = 32) and argon (M/z = 40); these are gases that were dissolved in the sample. The first peak (1.15-2.92 min) is a mixture of moisture (M/z = 18Da) and HCl (M/z = 36Da and 38Da) or $(H_3O^+)Cl^-(H_2O)_n$, as indicated in MS (Fig 12b). The major compound appeared at 5.433 min (Fig 12c) and was identified as 4-octene (Fig 12d). At 12.52 min (Fig 12e) 5-methyl-2-decane on the chromatograph (Fig 12f), then 12.76 min (Fig 12g) showed 2-ethyl-1,3-dimethylbenzene (Fig 12h). The next compound was at 12.98 min (Fig 12i) 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 (Fig 12j) at 30.8 min diisooctyl phthalate. The last compound was identified as 1,2-benzenedicarboxylic acid ester (30.94 min), mono (2-ethylhexyl) phthalate (Fig 12k). Fig 12 shows the MS of the major chemicals in the chromatogram compared with the most similar MS of chemicals from NIST library. The peak's RT also indicated on the corresponding MS.

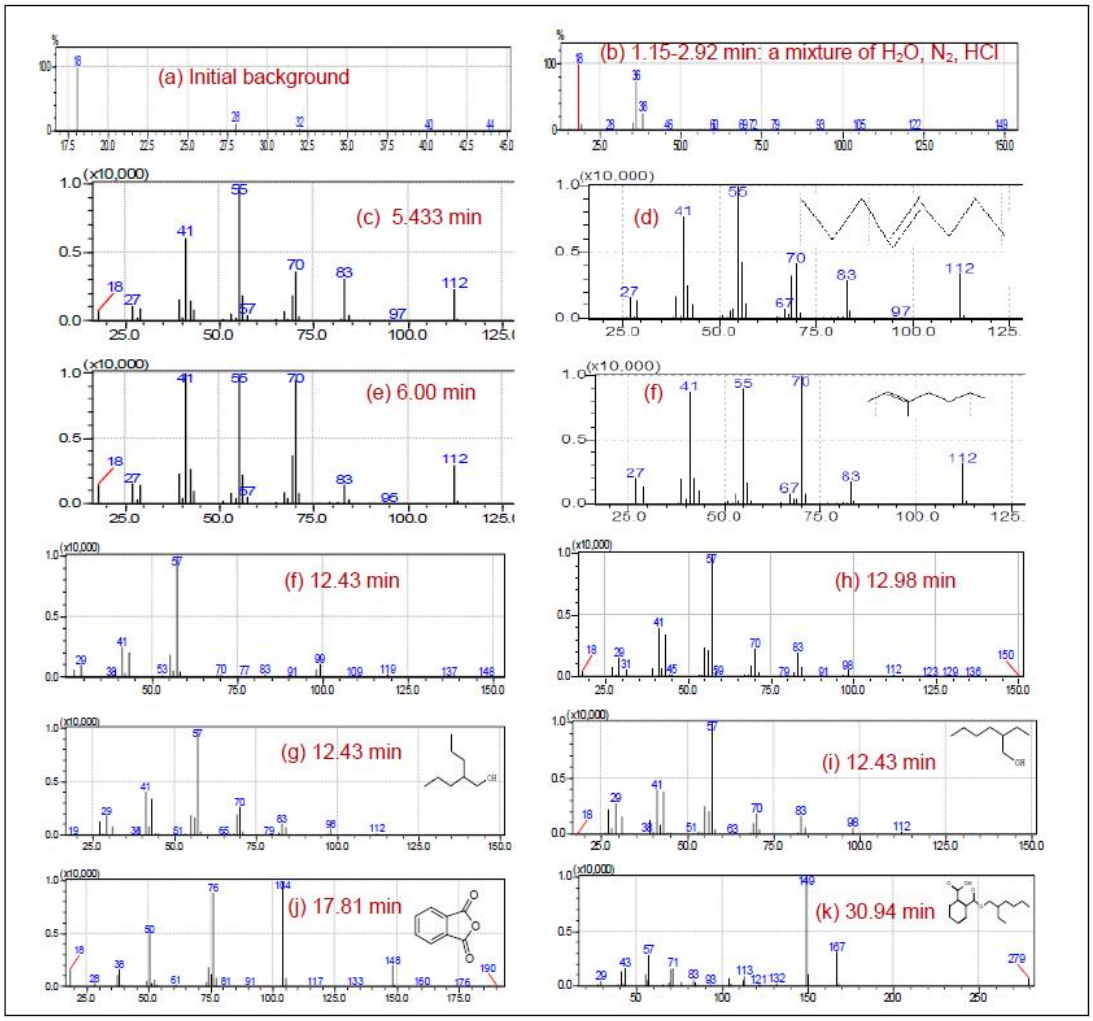


Fig 12. Chromatograph of major compounds in Sample 3. The retention time and the structure of compound are indicated in MS.

3.2.5. Sample 4

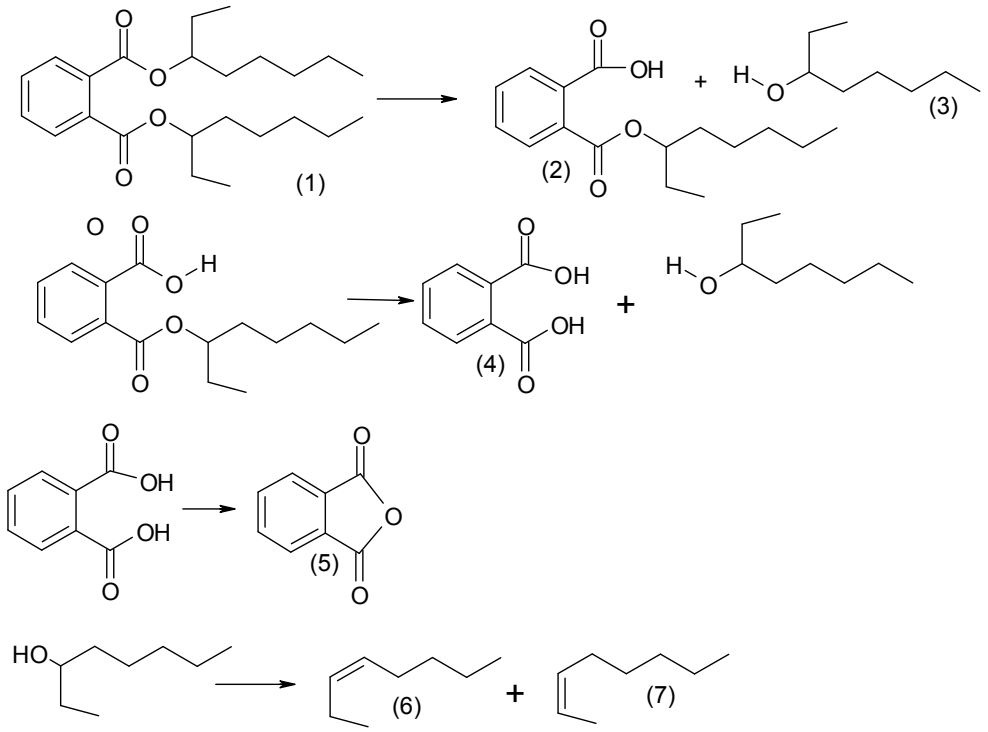
The chromatogram (Fig 9 Sample 4) shows at 1.16 min a mixture of water, HCl, and C5 isomers. At 1.59 min the concentration of moisture and HCl decreased very much, however, the C_5 compounds continued to elute, 1-pentene (mp 30°C) was visible, the mixture of pentene and HCl was recognized by the NIST library as 2-chlorpentane (bp 98°C) which must have 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 8.00 min C_8 isomers were identified (4-octene). After 8 min also the C_8 isomers were eluting; these isomers possessed more than one double bond, for example, the scan at 8.33 min identified it as 3,5-octadiene. From 8.50 min we began to observe C_9 isomers, for example the scan at the top of peak at 8.57 min was identified as 3,5,5-trimethylcyclohexene. Xylenes (benzylic C_8) appeared from 8.63 to 9.10 min. At 9.13 min C_9 isomers began to appear, the scan on top of the peak at 9.24 min was identified as 4-nonene. The peak at 9.50 min indicated the presence of 1-ethenyl-3-methylene-cyclopentene. At 9.90 min 7-methyl-3-octene, and 2,4-dimethyl-2,4-heptadiene appeared at

10.45-10.57min. From 10.88 to 10.58 min 2,5-diethyltetrahydrofuran, a cyclic ether, and after it came 2,2'-bioxepane. C_{10} isomers were 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 peak centered at 12.72 min was 2,6,6-trimethylbicyclo[3.1.1]heptane $C_{10}H_{18}$. Brominated compounds also were identified in the products of pyrolysis, for example, the peak at 13.00 min was 4-bromoheptane $C_7H_{15}Br$. The peak at 13.21 to 13.66 min was 2-propyl-1-pentanol or 2-ethyl-1-hexanol $C_8H_{18}O$ since their MS is very near to each other judgment is difficult. The lower section of the peak at 13.80 min identified as 6,8-nonadien-2-one, 6-methyl-5-(1-methylethylidene), $C_{13}H_{20}O$. The compound at 26.97 min was isobutyl laurate dodecanoic acid $C_{16}H_{32}O_2$, the compound at 27.74 min was 1-propylpentyl laurate $C_{20}H_{40}O_2$; and at 27.73 min mono(2-ethylhexyl) phthalate $C_{16}H_{22}O_4$, at 27.98 min eicosanoic acid, $C_{20}H_{40}O_2$, at 28.08 to 28.15 min identified as 2,6-ditert-butyl-4-methylphenyl-1-(1-hydroxy-2-methylpropyl)cyclopropanecarboxylate $C_{23}H_{36}O_3$. The compound at 28.28 min was identified as silane, dimethyl(2-propylphenoxy) butoxy- $C_{15}H_{26}O_2Si$, the compound at 28.27 to 28.46 min was identified as succinic acid, 2-ethylhexyl undecyl ester $C_{23}H_{44}O_4$, the compound at 29.15 min was identified as (3-beta)- 14-methylcholest-7-en-3-ol $C_{28}H_{48}O$, the compound at 29.68 min 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 30.62 min was identified as 2-ethylhexyl undecyl ester, fumaric acid $C_{23}H_{42}O_4$, the compound at 30.87 min was identified as 2-chloroethyl decyl ester phthalic acid $C_{20}H_{29}ClO_4$.

3.2.6. Sample 15

The appearances of the chromatograms of samples 5 to 14 were similar. Therefore, an extended analysis of every sample was omitted. As the chromatogram (Fig 9 sample 15) showed 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 2, (1)) and polyesters may lead to compounds such as mono-(2-ethylhexyl)phthalate (Reaction 2, (2)), 2-ethylhexanol (Reaction 2, (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 possible route for decomposition of 1,2-benzenedicarboxylic acid, di(2-ethylhexyl) ester to 1,2-benzenedicarboxylic acid, mono(2-ethylhexyl) ester, 2-ethyl-hexanol, 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 at section 3.3).
The content of the main peak at 1.34 min (Fig 8 Sample 15) is HCl and moisture (Fig 13, 1.34 min). The TIC at 1.48 also contains also moisture and HCl plus other chemicals. When the background was subtracted from the TIC, 2-methyl-butane a C_5 saturated hydrocarbon was identified. At 1.61 min 2,3-dimethylbutane C_6H_{14}, from 1.70-2.27 min a mixture of hexanes was viable. The high abundant materials at 2.41 min identified as benzene, C_6H_6. At 4.23 min toluene, and at 5.06 - 5.84 min 2-ethyl-1-hexene C_8H_{16}, at 5.85 min 3-dimethyl-1-hexene C_8H_{16} were identified. At 8.06 min ethyl-benzene C_8H_{10}, at 8.43 p-xylene C_8H_{10}, at 9.30 min m-xylene C_8H_{10}, at 11.42 min cumene C_9H_{12}, at 11.47 min to 11.62 min 4-chloro-2,4-dimethylhexane $C_8H_{17}Cl$. At 12.11 min benzonitrile C_7H_5N, at 12.21 min hemimellitene, 1,2,3-trimethyl benzene,C_9H_{12}, at 12.28 min undecane, $C_{11}H_{24}$ at 12.62 min 3,3-diethylpentane $C_{10}H_{22}$. It is hard to analyze after RT = 15 min because of super saturation of the column. Table 9 shows the detailed list of the 50 major compounds in the sample 15.

3.2.7. Sample E

Sample E was selected for GC-MS analysis as a representative sample of the fourth stage of pyrolysis. The aqueous samples A to C were strongly acidic. However, TIC of sample E did not show any presence of HCl. The highest abundance of chemicals were: at 1.29 min allyl vinyl ether, at 2.18 min 1-pentene, at 2.50 min benzene, at 4.70 min toluene, 5.00 min octene, 7.90-9.40 xylene isomers, 9.60 min 2,4-dimethylhexane, 11.34 min ethyltouene,

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 15.90 1-Isopropylvinyl)benzene. Table 10 (appendix) shows the 50 major chemicals in the sample E.

3.3. The Solid Samples

The 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 TICs used to analyzed the solid samples (a to f).

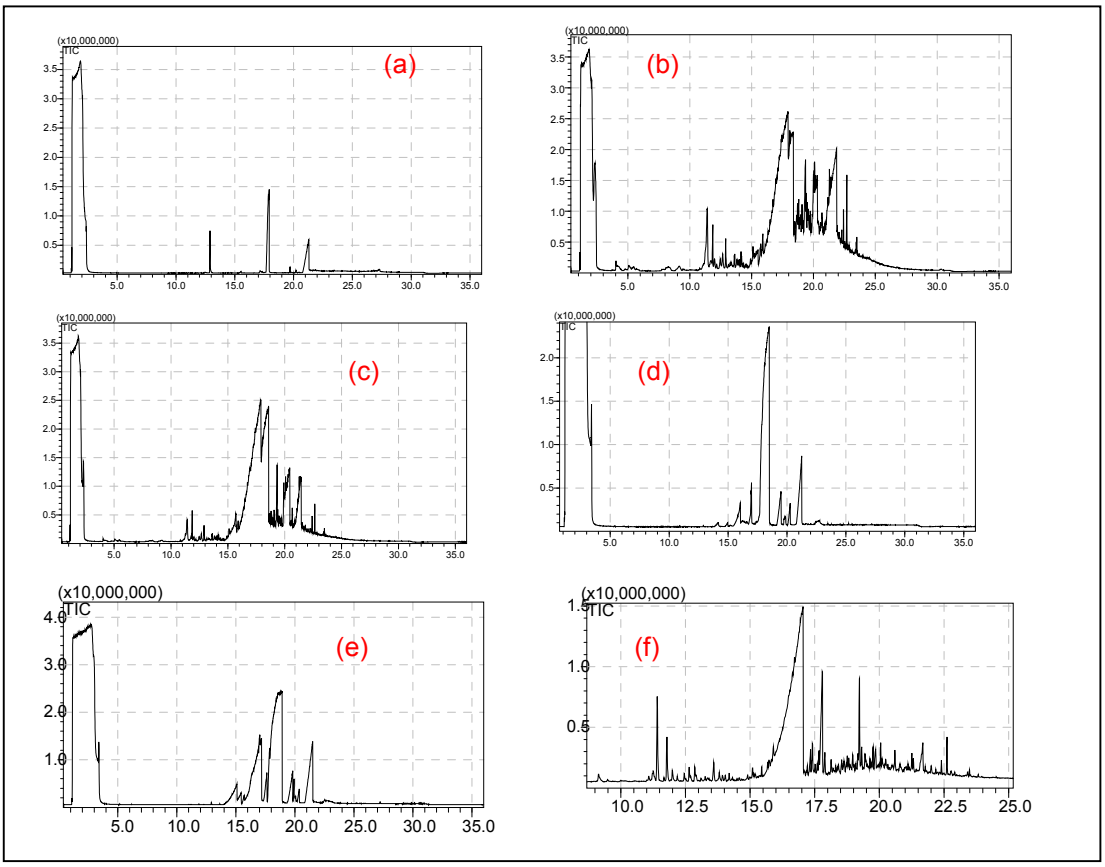


Fig 14. TIC of methanol soluble solids: (a) solids crystallized out of joint (Fig 2c); (b) Hexanes soluble parts of the solid collected from inside of condenser (Fig 3b); (c) crude solid precipitated in condenser; (d) Purified crystals (Fig 16e); (e) The solid precipitated in water (Fig 16 a); (f) solids soluble in hexanes (Fig 16 c), and its expansion (RT =9-25 min).

3.3.1. The sample crystallized outside of the joints

The solid samples resulted from the leak out of the distillates from the distillation head joints,

crystalized outside of receiver joints (Fig 2c) was soluble in the mixture methanol : water (90:20 v:v) and boiling water. Its aqueous solution was acidic. The sample was recrystallized from water (Fig 16c).The GC-MS of a few crude crystals dissolved in methanol (Fig 14a) showed three main picks. The pick at 12.82 min (Fig 15a) was identified as 2-propyl-pentanol (Fig 15b) or 2-ethyl-hexanol (Fig 15c). The TIC pick centered at 17.80 min (Fig 15d) was identified with phthalic anhydride (Fig 15e) or phthalic acid (Fig 15f); and the final peak located at 21.20 min (Fig 15g) was identified with di-(1-hexen-5-yl) ester $C_{20}H_{26}O_4$ (Fig 15 h).

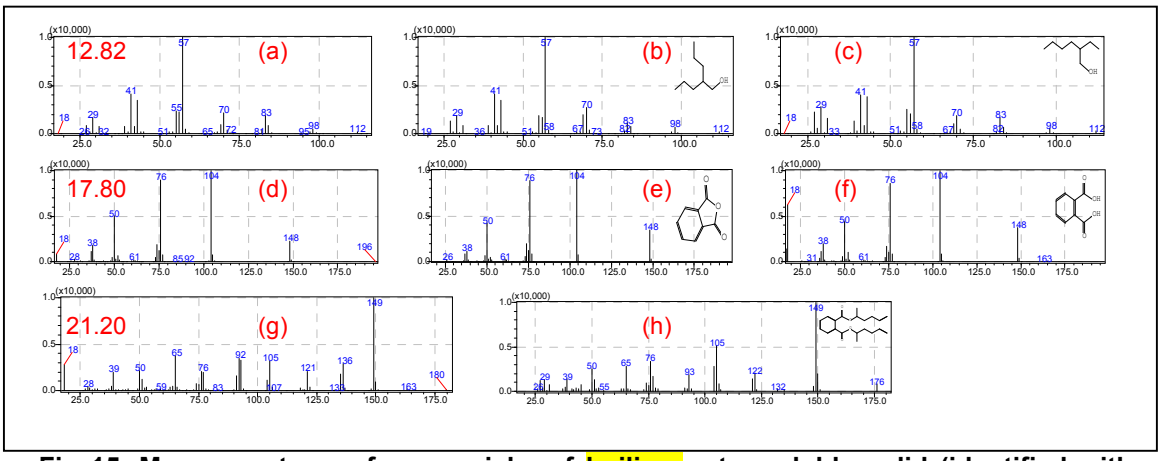
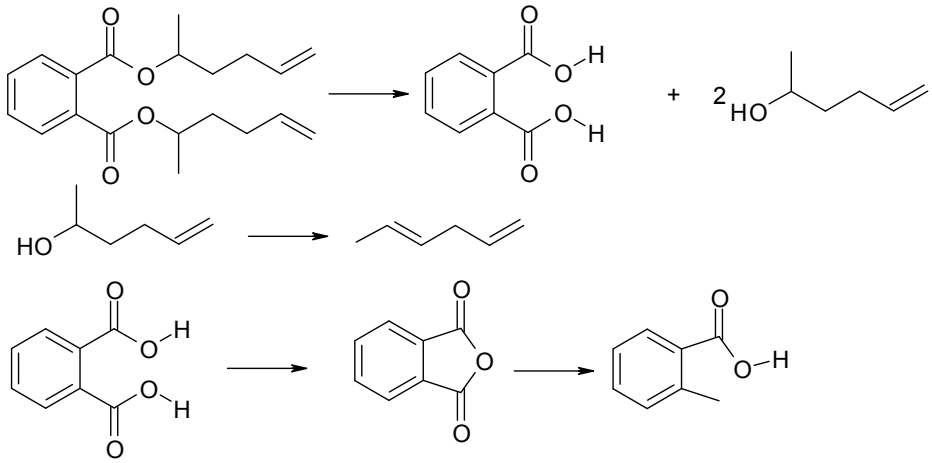


Fig 15. Mass spectrum of some picks of boiling-water-soluble solid (identified with their retention time (min)) and the most similar MS from NIST library for comparison.

The result of GC-MS (Fig 15a-h) indicated 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 (Reaction 3, step 1); , the alcohols by losing water converted to alkenes (Reaction 3, step 2). The acid is not stable over 210°C temperature then it converted to anhydride and other products (Reaction 3, step 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 distillate's 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 was also separated into two phases; part of this sample was hexanes soluble, red in color (Fig 16b), and most of the solid was insoluble in hexanes then precipitated (pale color solids). Both solutions were strongly acidic. After the water solution cooled down, amorphous and crystalline materials were visible in the aqueous layer and organic materials on the top layer (Fig 16c). However, there was no change in the hexanes solution (Fig 16d). Recrystallization of precipitated solid in agues solution produced crystals and amorphous materials (Fig 16e).

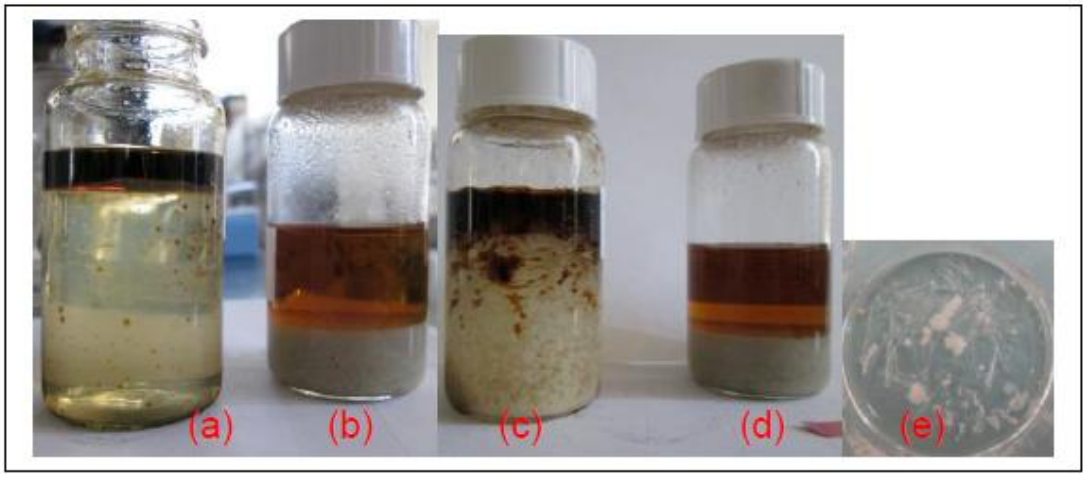


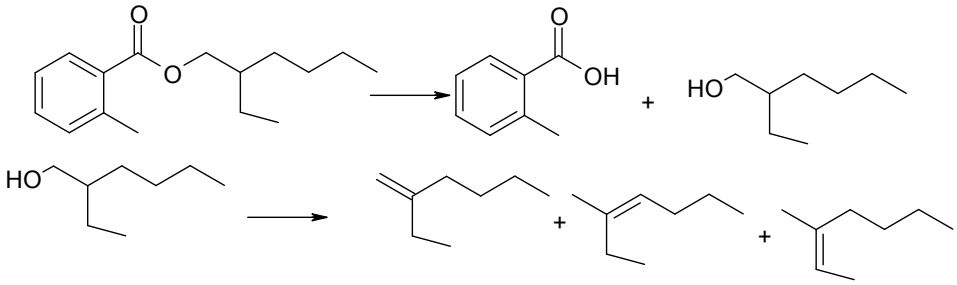
Fig 16. Solubility of solid products: (a) in hot water; (b) in hexanes; (c) precipitation and crystallization of the solids in water; (d) no change in hexanes solution; (e) shape of pure crystals in water.

3.3.3. Analysis of crude solids

The TIC of crude solid precipitate in in the condenser dissolved in methanol/water mixture (90:10) showed several chemicals (Fig 14b). As Fig 16a and b show, these solids are contaminated with liquid distillates. The first wide and high peak in TIC (Fig 14b) relates to solvent, methanol and water mixture (90/10); the end shoulder at 2.28 min was hydrogen chloride. The first major peak (11.25 min) was cumene or Isopropylbenzene C_9H_{12}, and the one at (11.41 min) was 3-chloro-3-methylheptane, $C_8H_{17}Cl$, or $C_{11}H_{22}$. The sharp peak at 11.86 min was benzonitrile C_7H_5N, and next small one (12.66 min) was 1-methyl-3-ethylbenzene C_9H_{12}, and the next to it (12.89 min) was 2-propyl-1-pentanol $C_8H_{18}O$. Fig 17 (appendix) shows the MS of the major compound in the sample and the MS of most similar compounds to it searched from NIST library (Fig 17 second column).

The major compound of this chromatogram located between 15-24 min consisted of phthalic esters derivatives. At 15.30 min benzoic acid $C_7H_6O_2$, at 17.03 min 2-methylbenzoic acid $C_8H_8O_2$, at 18.10 min to 18.53 min phthalic anhydride $C_8H_4O_3$, at 19.32 min 2,6-dimethylnaphthalene $C_{12}H_{12}$, at 19.34 min diphenyl methane, at 19.91 min N-ethylphthalimide $C_{10}H_9NO_2$, at 20.28 min phthalimide or phthalimidomethyl 3-methoxybenzoate, $C_{17}H_{13}NO_5$, at 20.38 - 20.43 min o-cyanobenzoic acid, $C_8H_5NO_2$, at 21.075 min to 21.43 min phthalic acid, di-(1-hexen-5-yl) ester $C_{20}H_{26}O_4$, at 22.63 min

ethylhexylbenzoate $C_{15}H_{22}O_2$, at 23.42 min o-toluic acid, 2-ethylhexyl ester $C_{16}H_{24}O_2$, were identified. Reaction 4 shows the origin of some chemicals found in the chromatogram.



Reaction 4. A schematic degradation of 2-ethylhexyl-2-methylbenzoate to 2-methylbenzoic acid and 2-ethylhexanol, then the alcohol to alkenes.

3.3.4. The clear crystals

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

3.3.5. The precipitated in water

The TIC of amorphous sample precipitated in water (Fig 14e) is very similar to the purified crystals (Section 3.3.4). MS shows the following chemicals: Benzoic acid (15.1 -17.1 min), 2-methyl benzoic acid (17.59 min), phthalic anhydride (17.69-19.93 min), 3-formyl-benzoic acid (19.40-19.81 min), phthalimide (19.93 min), phthalic acid, and di-(1-hexen-5-yl) ester (20.80-21.50). The results indicated that the amorphous material is a mixture composed of phthalic acid, benzoic acid, and their derivatives.

3.3.6. The hexane soluble

The TIC of hexane soluble portion of the precipitates in the condensers (Fig 14f) showed chemical content similar to the liquid fractions in addition to be saturated with slightly soluble components which were detected in section 3.3.5. The following is a list of the major chemicals in sample: 3-chloro-3-methylheptane (11.87 min), benzonitrile (12.03 min), benzoic acid (15.50-17.00), phthalic acid (17.74), dimethylnaphthalene (18.74), di-(1-hexen-5-yl) ester of phthalic acid (21.65), ethylhexyl benzoate (22.62). Table 11 contains a more extended list of the chemicals which were absorbed to the solids precipitated in the condenser.

4. CONCLUSION AND REMARKS

The results showed that parts of the pyrolysis products of LSGs are rich in many varieties of chlorinated compounds which are potentially hazardous to the environment and human health. Comparing TICs (Fig 9) 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 increased with time as observed in sample 15; the peak height and area of benzene was higher than combined HCl and moisture. All samples had three kinds of

materials, volatile organic hydrocarbons that are suitable as gasoline, visible in the chromatogram from 1.58 to 10 min mainly C_6 to C_{11} hydrocarbons; semi-volatile materials were visible after 11 min with carbons numbers higher than 12, and solid organic acids and esters that appeared 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 was 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 contained carbon compounds. However, above 800°C the residue was carbon free. Therefore, the nature, yields, and the chemical compositions of the liquids produced by pyrolysis of the waste gloves depended on the engineering of the process and the heating limitation of the reactor. Last but not least, the products of pyrolysis contained highly reactive chemicals; these materials were 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 the 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 derivative gases (C, C_2, C_3, C_4, and C_5). 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%) was due to production of some chlorinated hydrocarbons. In addition, a part of gloves mass is chlorine-free fillers and plasticizers which increased the yield of pyrolysis.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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