Oil fractions from the pyrolysis of diverse organic wastes: the different effects of conventional and microwave induced pyrolysis

D. Beneroso^a, J.M. Bermúdez^a, A. Arenillas^a, F. de la Peña^b, J.L. García^b, M.A. Prieto^b,
J.A. Menéndez^{a*}

^a *Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain*

^b *Centro de Investigaciones Biológicas, CSIC, C/ Ramiro de Maeztu, 9, 28040 Madrid, Spain*

* Corresponding author. Tel.: +34 985 118972; Fax: +34 985 297672

E-mail address: angelmd@incar.csic.es

Abstract

Several studies have dealt with the microwave-induced pyrolysis of organic residues as an effective technology for maximizing the production of syngas at the expense of the production of oily tars. This liquid fraction is composed of a complex mixture of organic compounds making it difficult to upgrade for use as a biofuel and containing hazardous compounds such as polycyclic aromatic hydrocarbons (PAH). In this study the effect of the type of residue (municipal solid wastes, sewage sludges, plastic wastes and agroresidues) and the heating mechanism on the product distribution within the oil fraction has been investigated by means of GC-MS technique. Two different approaches have been performed: direct GC-MS analysis and methanolysed-oils GC-MS analysis, the later determining the non-volatile compounds. In general, quite different distributions are attained when microwave pyrolysis is conducted, providing lighter compounds. In some cases, such as the plastic-derived oil, microwave pyrolysis lead to a potential source of chemicals such as benzene, toluene and xylenes.

Keywords Microwave pyrolysis, Polycyclic Aromatic Hydrocarbons, Waste management, Tar reduction

1. Introduction

Climate change and its relationship with CO₂ emissions has become an issue of major concern in recent years [1]. Although several efforts are being made to bring this phenomenon under control, the problem continues to grow. According to the World Energy Outlook of the International Energy Agency, the energy demand is expected to increase until 2035 and the associated CO₂ emissions to rise by 20% [2]. Indeed, fossil fuels will continue to be the primary source of energy generation in the short to medium term. However, in the same report this organization states that government policies can influence the pace of fossil fuel consumption. Governments have already taken concrete decisions to reduce the risks associated with fossil fuel emissions. Some examples are the Climate Action Plan in USA or the European Strategic Energy Technology Plan of the European Union [3,4]. In the case of the EU plan, one of its objectives is that 14% of the European energy mix should come from cost-competitive and sustainable bioenergy by 2020. Accordingly, technologies such as pyrolysis or gasification are going to play a key role in the development of this cost-competitive bioenergy in the near future [4].

Pyrolysis is a process in which organic matter is thermally decomposed without the use of oxidizing agents to yield three different fractions: a solid residue commonly known as char, a liquid oily fraction (tar) and a gaseous fraction. Gasification is a process which begins with a pyrolysis step that is then followed by the gasification of char and the reforming and cracking of tars and light hydrocarbons by a gasifying component, such as steam or oxygen. As a consequence, gasification usually yields higher amounts of gas than pyrolysis [5].

1 One of the main problems with both technologies is the production of a large amount of
2 tars [6]. This liquid fraction is a complex mixture of organic chemicals largely
3 composed of aromatic and polycyclic aromatic hydrocarbons that can be hazardous for
4 health and the environment. Moreover, they can cause problems that affect the process
5 itself including the fouling of engines and the deactivation of catalysts [7,8]. For these
6 reasons, research into biomass pyrolysis and gasification is looking for ways to decrease
7 the production of tars or, at least to improve their quality, by keeping the proportions of
8 complex compounds like polycyclic aromatic hydrocarbons (PAH) down to a minimum.

9 For this reason, the use of microwave heating is seen as an appealing alternative since
10 the main feature of microwave-induced pyrolysis (MIP) is its ability to maximize the
11 production of gas and minimize that of tars [9]. This tendency has been tested with
12 many different types of residues, including algae, municipal solid wastes, agricultural
13 wastes, sewage sludge and automotive wastes [10-13]. However, so far the effect of
14 microwaves upon the quality of the tars has not been given serious consideration. Some
15 studies have pointed out that, while MIP could serve to minimize the production of
16 PAH [14], the type of residue used might also be an influential factor. In this regard, the
17 gaseous composition from the MIP seems to be very similar regardless of the residue
18 pyrolysed with few exceptions [12,13,15,16], syngas (H_2+CO), CO_2 and light
19 hydrocarbons being the most common gaseous species found. On the other hand, the
20 influence of the type of residue on oil composition is much more prominent. For this
21 reason, the trends observed in the production of PAH by MIP in the study of
22 Domínguez *et al.* [14] cannot be generalized without carrying out a deeper study of the
23 process with several types of wastes. It is the aim of the present study to make up for
24 this shortcoming by gaining further insight into the influence of microwave heating on

the composition of the tars produced during the pyrolysis of different types of organic residues as a continuation of a previous study in which the suitability of several organic wastes was examined in order to maximize the production of syngas for further bioplastics production [17].

2. Experimental

2.1 Materials

Four different samples, provided by BEFESA Gestión de Residuos Industriales S. L. (Seville, Spain), were selected for this study:

- An organic fraction from a municipal solid waste, dried and partially cleaned from inerts, such as glass and metals. After this pre-treatment, the fraction size was reduced to 1-3 mm. This sample has been labelled MSWd.
- Dried sewage sludge. This sample was collected from a wastewater plant in Seville. The sludge, after being subjected to secondary treatment, was dried to facilitate transportation. After being dried, the sample was milled down to a size range of 1-3 mm. This sample has been labelled SSd.
- A plastic fraction from a municipal solid waste. This sample, a complex mixture of plastic residues, was obtained from the same landfill site in Seville. The fraction was milled to 1-3 mm and has been labelled PLA.
- An agricultural residue. This sample was obtained from a biodiesel production plant located in Salamanca (Spain) and is composed of straw. The sample was also milled down to a size range of 1-3 mm. This sample has been labelled STR.

The moisture, ash content and volatile matter data of the residues were obtained by means of a LECO TGA-601. To perform the ultimate analysis, a LECO-CHNS-932 micro-analyzer and a LECO-TF-900 furnace were used. The metallic content of the ashes was determined by means of ICP-MS analysis. First, the samples were dissolved in inorganic acids (HNO_3 4N and concentrated HCl) and digested using microwave heating in a MILESTONE ETHOS 1 oven at 600 W during 35 min. Identification of the elements was carried out on an *Agilent 7700x* using a Ar plasma. An external calibration method between 0 and 1000 ppb internal standard (Sc) and a collision cell of He (to eliminate possible matrix interferences) was used to determine the concentration of metals. The results of this characterization are presented in Table 1.

2.2 Pyrolysis techniques

Conventional pyrolysis (CP) was performed at 800 °C in an electric furnace. Approximately 4 g of sample was introduced into a quartz reactor. First, the reactor was placed outside the furnace and purged with N_2 for 30 min at a flow rate of 50 mL min^{-1} to ensure an oxygen-free atmosphere. Meanwhile, the furnace was heated up to 800 °C. Once the reactor had been purged and the electric furnace had reached the desired temperature, the N_2 flow was reduced to 10 mL min^{-1} and the reactor was introduced into the furnace for pyrolysis, the duration of which was 1 h. The use of such a low flow rate favours secondary reactions of tar allowing for a maximum syngas production [17,18]. The volatiles evolved during pyrolysis were forced to pass through a condensing system (cooled by a cryogenic solution of water and NaCl) where the condensable compounds were removed from the gaseous fraction. Both the reactor and

the condensing system were weighed before and after the pyrolysis experiment to determine the solid and liquid yields (respectively). The gas yield was determined by difference. Each experiment was performed in duplicate to check the repeatability and the errors came to less than 6% both for the yields and the gas composition [17].

Microwave-induced pyrolysis (MIP) was performed using a microwave oven consisting of a microwave magnetron with a maximum output power of 2 kW operating at 2450 MHz and a single mode cavity where the sample-containing quartz reactor was placed. As in conventional pyrolysis, the reactor was purged with N₂ for 30 min at a flow rate of 50 mL min⁻¹. The flow rate was then reduced to 10 mL min⁻¹ and the microwave irradiation was switched on and regulated until a temperature of 800 °C was reached. The reflected power was regulated by means of tuning screws until it reached zero. The same system as that used in CP was used to collect the liquid fraction.

Owing to the poor capacity of organic wastes used in this study to absorb microwaves, it was necessary to use a microwave receptor material to induce the pyrolysis [12]. For the purpose of this study, the char obtained from a previous pyrolysis at the same temperature (hence, very unlikely to release any volatiles at 800 °C) was employed as a microwave receptor at a receptor – to –feedstock mass ratio of 0.3:1.

2.3 Characterization of the oil fractions

To characterize the oils, a semi-quantitative study was carried out by calculating the percentage of area of the chromatographic peaks. Two different sample preparations were performed before the GC-MS analysis:

- In the first, anhydrous sodium sulfate (Na_2SO_4) was added to the condensed oil fraction to remove all traces of water, and injected directly into the GC-MS in order to identify the volatile compounds.

- In the second, the following methanolysis step was included. 2 mL of methanol containing 15 % sulfuric acid and 0.5 mg/mL of 3-methylbenzoic acid (internal standard), was introduced, after dehydration of the oil with Na_2SO_4 , followed by an incubation period of 7 h at 80 °C. After cooling, 1 mL of demineralized water and 1 mL of chloroform were added and the organic phase was analyzed by GC-MS. During the methanolysis step, the non-volatile compounds (mainly fatty acids) were turned into methyl ester derivatives, which are volatile compounds and can be easily identified by GC-MS.

All the samples were analyzed by GC-MS using an Agilent 7890A gas chromatograph (Agilent Technologies, Palo Alto, California, USA) coupled to an Agilent 5975C mass detector (electron ionization, 70 eV) (Agilent Technologies, Palo Alto, California, USA) and equipped with a 30 m $\times$ 0.25 mm i.d. capillary column (0.25 μm film thickness) HP-5 (methyl silicone bonded) (Agilent Technologies). The working conditions for the first sample (volatile compounds) were as follows: a split ratio of 50:1 (0.02 μL of oil sample in 1 μL of dichloromethane) and an injector temperature of 350 °C; a column temperature of 40 °C for 3 min, which was then increased to 325 °C at 7 °C min^{-1} . The methanolysed samples were analyzed using the same equipment under the following working conditions: a split ratio of 20:1 (0.25 μL of oil sample) an injector temperature of 350 °C; a column temperature of 40 °C for 3 min, which was then heated to 325 °C at

20 °C min⁻¹. Blank analyses were also conducted to prevent possible procedural contaminants to be taken into account in the oil characterization.

The mass spectra and retention data were used to identify the compounds by comparing them with those of the standard in the NIST Mass Spectral Database. Those compounds were identified with a probability higher than 80%. The semi-quantification study was conducted on the basis of the percentage of area under each peak compared to the total amount of area under all the peaks in the chromatogram. The relative standard deviations obtained for testing the reproducibility for the peak areas came to less than 4% and the retention times to less than 1%.

3. Results and discussion

The data related to the ultimate composition, proximate analysis, H/C ratio and the ash metallic analysis of the different selected residues are presented in Table 1. The results reveal significant differences in the nature of the residues, which range from low carbon and high ash contents in the case of the MSW fraction, to high carbon and low ash contents, in the case of the PLA fraction. Furthermore, the straw sample and the organic fraction from the municipal solid waste have a high organic oxygen concentration. The values obtained for the H/C atomic ratio are high in the cases of MSWd, PLA and SSd fractions reflecting the marked aliphatic character of these wastes and the presence of long chains of -CH₂- groups. The O/C atomic ratio values of the wastes, which range from 0.43 to 0.70, are very similar to the O/C values of the biomass samples [19], with

the exception of the PLA fraction, which has quite a low ratio, which is indicative of a high heating value.

Table 2 shows the solid, oil and gas yields resulting from the residues during conventional pyrolysis and microwave pyrolysis. MIP has been reported to be an effective way to maximize the gas yield from the pyrolysis of biomass and organic wastes [12,13,15]. This finding is in agreement with the yields presented in Table 2 in the cases of MSWd and STR, with oil showing the lowest yield for all the residues subjected to MIP, the resulting values ranging between 7 and 34 wt.%. Nevertheless, the SSd and PLA fractions produce slightly more gas in the case of CP. This could be due to the fact that these fractions produce more hydrocarbons, such as CH₄, C₂H₄, C₂H₆, C₃H₈ or C₃H₆, which can be easily cracked into hydrogen, smaller hydrocarbons and coke under microwave radiation, resulting in an increase in the solid fraction yield [20], as is shown by Reactions 1 and 2 below. However, the increase in the solid yield is also a consequence of the cracking of the oil fraction components, which means that the oil fraction yield decreases in all cases.

With respect to the composition of the oil fraction, GC-MS analysis revealed that both CP and MIP derived oils were composed of a mixture of low and high molecular weight compounds. As an example, the chromatograms of MSWd-derived oils from both preparation methods are presented in Fig. 1. In the case of chromatograms following the first preparation method (without methanolysis step), the compounds detected are listed

1 in the Supplementary Material. Fig. 2 shows the weight distribution (in molecular
2 weight) of the compounds present in the oils, which depends on the pyrolysed residue
3 and the heating mechanism. It should be pointed out that the values of relative
4 abundance do not represent the real concentrations of the compounds. Rather, they
5 indicate the different compositions of the resulting oils.

6 Fig. 2(a) shows that in the case of the MSWd fraction, MIP induces lesser amounts of
7 oils in all the molecular weight intervals studied, with the exception of the 250 – 300
8 g/mol interval. During the microwave-induced pyrolysis of MSWd, it was observed that
9 the production of volatiles was much more rapid and steeper compared to the other
10 residues. This may have prevented the volatiles from being cracked to a certain extent,
11 giving rise to heavier oil compounds. Nevertheless, when the results from CP and MIP
12 are compared, the distribution shapes are very similar in both cases.

13 However, the distribution shapes of the different heating mechanisms are not always
14 similar, since here the distribution also depends on the type of pyrolysed residue. In the
15 case of the SSd fraction, according to its oil weight distribution (Fig. 2(b)), MIP
16 produces lighter compounds as the distribution shifts to low molecular weights, in
17 contrast to CP, which favours the production of heavier compounds, such as siloxanes,
18 fatty acids and large amides. A similar distribution can be observed in the case of the
19 PLA fraction, where most of the MIP oil compounds are generated in the interval 100 –
20 150 g/mol, with ethylbenzene and styrene as the main compounds. These results
21 contrast with CP that favours the production of large-chain olefins, such as
22 eicosadienes. In the case of the STR fraction both heating mechanisms favour lighter oil
23 compounds, especially CP which produces large quantities of acetic acid and acetol.

Pyrolysis oils are complex mixtures of organic compounds with a wide variety of chemical groups. To qualitatively describe their composition, the compounds identified in the oils have been grouped into the following classes: BTX (benzene, toluene, xylene and their alkyl-derivatives), PAH (polycyclic aromatic hydrocarbons), aliphatics (alkanes and alkenes), oxygenates (alcohols, ketones, esters and their derivatives), nitrogenates (amides, nitriles and N-heterocyclic compounds), fatty acids and, where applicable, siloxanes.

Fig. 3 shows the proportions of the different classes of compounds identified in the pyrolysis oils. Large amounts of BTX compounds were obtained from the SSd and PLA fractions under MIP. Of particular interest is the large amount of BTX detected in the plastic derived oil. PLA is composed basically of polymeric chains and when it was subjected to MIP, the amount of aliphatic oil was reduced compared to the oil from CP that favours the production of aromatic compounds (BTX). Aromatics are likely to be formed via Diels–Alder type secondary reactions, which involve the cyclisation of alkenes (produced from the thermal degradation of the PLA fraction) to form aromatic hydrocarbons (first step in Reaction 3, see below) [21]. These secondary reactions are likely to occur in MIP as reported in other pyrolysis processes [14,21,22]. Furthermore, the products from Diels–Alder reactions may undergo condensation to yield PAH when the temperature is high enough, ca. 700 °C (second and third steps in Reaction 3) [22]. The increase observed in the PAH content in the PLA-derived oil under microwave pyrolysis can also be explained by Reaction 3, since microwaves generate *hot spots* inside the residue which locally induce temperatures much higher than 800 °C [23].

2
3 There is also an increase in the PAH content in the oil from the STR agroresidue. In this
4 case, no polycyclic aromatic hydrocarbons were detected under CP. However, MIP
5 generates naphthalene and low amounts of methylnaphthalene, fluorene and anthracene.
6 These compounds have been previously detected in the oil derived from the MIP of
7 agroresidues [11]. They are probably produced via reactions similar to Reaction 3
8 involving polymeric derived olefins from the lignocellulosic structures and
9 deoxygenation reactions (carbonyl and methoxy groups are removed) that yield more
10 stable aromatic species [24], as reported in the case of wood waste pyrolysis at high
11 temperature [22].

12 Nevertheless, MIP does not always increase the amount of PAH and the higher local
13 temperatures during MIP are not the only factor responsible for the production of PAH.
14 The type of pyrolysed substrate also has an influence. Fig. 2(a) and 2(b) show that both
15 the MSWd and SSd fractions produce lower amounts of PAH under MIP than under CP.
16 This reduction has already been reported for the MIP of different sewage sludges [25].

17 The differences in PAH contents depend on the type of residue. Some residues have a
18 highly polymeric nature (e.g., plastics), and are more easily converted into dienes and
19 olefinic structures (Fig. 4). They are able therefore to overcome Reaction 3 - type
20 reactions that generate PAH compounds. However, this is not the case of MSWd and
21 SSd, which are heterogeneous materials. Lignocellulosics also have a polymeric nature

but in this case PAH compounds are favored by the deoxygenation of furans, phenols and cyclopentadienes during the thermal degradation of cellulose [26].

Although the PAH concentration increases in the oils from PLA and STR as a result of MIP, no PAH carcinogens, (i.e., benz[*a*][8]anthracene, benzo[*a*]pyrene and dibenz[*a,h*]anthracene [27]), were detected in the oil product, none of the typical fragments from those PAH within the NIST database were observed during the mass spectrometry analysis under the experimental protocol used.

With respect to the aliphatic compounds present in the oils, the total yield was very low in the case of the SSd and STR fractions. However, this value reached nearly 20% in the MSWd fraction. A common observation is that these aliphatics consist of straight long chain hydrocarbons ($>C_{10}$), which represent an potential source of kerosene and diesel. The PLA fraction shows the largest amount of aliphatics, especially from CP (40%) where the formation of alkenes is clearly promoted to the detriment of alkanes in the C_{12} – C_{20} range. During microwave pyrolysis, the aliphatics content drops to 20% in favour of aromatics.

Most of the oxygenated compounds are ketones, esters and alcohols, the concentration of which depend on the nature of the residue and the heating mechanism employed. The oxygenates present in the oil produced by conventional and microwave pyrolysis of MSWd are mainly alkyl cyclopentenones, aliphatic and aromatic ketones. However, no ketones were observed in the SSd-derived oil, the major oxygenates being esters and aromatic alcohols. Nevertheless a significant decrease in the yield of the oxygenates occurred in the case of MIP. With respect to the PLA-derived oil, CP yielded two main long chain alcohols (1-eicosanol and 1-pentacosanol), although with microwave

pyrolysis the presence of oxygenates in the oil is practically excluded. In the case of the STR fraction, oxygenates are by far the most important group, especially during CP, which is in accordance with the high oxygen content of lignocellulosic materials as in this case. The conventional pyrolysis of STR produces large quantities of acetic acid and ketones, whereas MIP promotes the production of phenol and phenol-derivatives.

Nitrogen-containing compounds are present especially in the oils from SSd, since this fraction initially contains a large amount of nitrogen compared to the other residues. The compounds detected in the oils from SSd comprised long chain aliphatic amides in the case of CP and nitriles, pyridine, pyrrole and their derivatives in MIP. Furthermore, a large quantity of siloxanes was detected in the SSd-derived oil, as is usually the case with biogas and sewage sludges [28].

Another important constituent of the pyrolysis oils are fatty acids. It can be seen from Fig. 3, that the SSd fraction does not produce fatty acids during MIP in contrast with its high content under CP. Because fatty acids are high molecular weight long chains, a GC-MS analysis was performed after a methanolysis step in order to identify non-volatile compounds that were not detected by GC-MS. The results of these analyses for each residue derived-oil are presented in Table 3. Within the MSWd fraction, palmitic and oleic acids were the most relevant compounds. The corresponding methyl esters were the main compounds in the oils from SSd. These compounds are of special interest owing to the fact that they can be used as source of biodiesel or even as platform molecules that can be converted into a variety of fuel additives through catalytic transformations [29]. Similar results were obtained from an analysis of the oil from the STR fraction after microwave pyrolysis. Here palmitic, linoleic, levulinic and

tetradecanoic acid methyl esters made up most of the compounds detected. In the case of the oils from PLA, the resulting distributions between CP and MIP differ considerably, since the main components are benzoic and palmitic acids methyl esters in the case of conventional pyrolysis, but methoxyethyl benzene and ethylbenzene in the case of microwave pyrolysis. MIP gives rise to a wider distribution of products and generates alkyl-derivatives of BTX compounds, as can be seen from Fig. 3.

It is important to point out that the oil yield from MIP is always lower than that obtained from CP, suggesting that the production of identified chemicals can be reduced. This is the case of MSWd, for which a rough estimation predicts a yield of PAH from conventional pyrolysis of around 70 mg/g_{waste} against 15 mg/g_{waste} from MIP.

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Figure captions

Figure 1. Chromatograms of MSWd-derived oils from CP and MIP.

Figure 2. Molecular weight distribution of compounds according to their relative abundances in the oil fraction obtained from (a) a municipal solid waste (MSWd); (b) a sewage sludge (SSd); (c) a plastic solid waste (PLA) and (d) agroresidues (STR).

Figure 3. Relative abundance of different groups of compounds found in the oil fraction obtained from (a) a municipal solid waste (MSWd); (b) a sewage sludge (SSd); (c) a plastic solid waste (PLA) and (d) Agroresidues (STR).

Figure 4. A typical polymer beta scission mechanism.

Table 1. Chemical characteristics of the selected residues [17].

	Proximate Analysis (wt.%)			Ultimate Analysis (wt.%) ^a							Metal content of ashes (mg kg ⁻¹)						
	MC	Ash ^a	VM ^a	C	H	N	S	O	H/C atomic	O/C atomic	Fe	Zn	Cu	Cr	Mn	Pb	Ni
MSWd	2.8	27.7	61.1	36.0	5.8	1.6	0.2	33.8	1.9	0.7	8896	183	45	59	83	31	18
SSd	3.4	15.4	74.5	43.8	6.1	9.7	0.1	24.9	1.7	0.4	2985	460	153	12	40	2	3
PLA	1.3	8.9	88.9	70.9	9.7	1.2	0.5	9.1	1.6	0.1	1099	73	51	73	19	5	25
STR	11.5	6.3	76.2	45.0	5.0	1.6	0.0	42.0	1.3	0.7	287	7	0	0	18	<i>tr</i>	<i>tr</i>

^a Dry basis; MC: Moisture content; VM: volatile matter content; *tr*: traces (<0.1 mg kg⁻¹).

Table 2. Fraction yields obtained from the conventional (CP) and microwave-induced (MIP) pyrolysis of different residues at 800 °C [17].

Residue	Solid yield (wt.%)		Oil yield (wt.%)		Gas yield (wt.%)	
	CP	MIP	CP	MIP	CP	MIP
MSWd	40.2	43.9	23.7	7.8	36.1	48.3
SSd	31.3	32.8	34.7	34.3	34.0	32.9
STR	24.5	22.8	37.9	21.3	37.6	55.9
PLA	11.2	35.2	36.8	20.3	53.0	44.5

Table 3. Relative abundances of compounds detected in the oil fraction by means of methanolysis.

MSWd – CP			MSWd - MIP		
Retention time (min)	Compound	Percentage quantified area	Retention time (min)	Compound	Percentage quantified area
5.54	Heptene	2.31	5.54	Heptene	3.80
8.39	Benzoic acid	2.93	8.39	Benzoic acid	2.11
10.12	Cyclohexasiloxane	11.87	10.12	Cyclohexasiloxane	16.16
11.29	Cycloheptasiloxane	7.71	11.29	Cycloheptasiloxane	16.22
12.70	Tetradecanoic acid	1.95	13.80	Palmitic acid	27.01
13.79	Palmitic acid	29.68	14.67	Oleic acid	21.28
14.68	Oleic acid	27.29	14.78	Stearic acid	13.42
14.78	Stearic acid	14.24			
15.08	Pyrene	2.02			

SSd – CP			SSd - MIP		
Retention time (min)	Compound	Percentage quantified area	Retention time (min)	Compound	Percentage quantified area
4.41	2-Butenoic acid, methyl ester	2.80	4.45	Toluene	6.90
4.60	3-Methyl butanoic acid, methyl ester	2.02	4.60	3-Methyl butanoic acid, methyl ester	2.31
5.93	2-Pentenoic acid, methyl ester	5.21	5.82	Ethyl benzene	1.82
6.19	4-Methyl Pentanoic acid, methyl ester	0.81	5.93	2-Pentenoic acid, methyl ester	7.26
7.30	Octamethyl cyclotetrasiloxane	11.37	6.19	4-Methyl Pentanoic acid, methyl ester	2.03
7.81	Succinic acid, dimethyl ester	2.02	6.98	Propyl benzene	0.79
8.09	Butanedioic acid, methyl ester	0.63	7.30	Octamethyl cyclotetrasiloxane	6.27
8.58	Benzenemethanol	1.17	7.39	Decane	0.55
8.72	Decamethyl cyclopentasiloxane	1.55	7.53	1 Methoxyethyl benzene	7.12
9.12	Phenylacetic acid, methyl ester	0.88	7.84	Succinic acid, dimethyl ester	1.20

9.26	Naphthalene	0.62	8.12	2-Methyl succinic acid, dimethyl ester	0.66
11.56	Bis (1,1 Dimethylethyl) Phenol	0.71	8.27	1-Undecene	0.78
12.69	Tetradecanoic acid, methyl ester	3.88	8.34	Undecane	0.86
13.69	Oleic acid, methyl ester	9.73	8.46	Benzoic acid, methyl ester	1.07
13.78	Palmitic acid, methyl ester	21.89	8.72	Decamethyl cyclopentasiloxane	0.65
14.28	Heptadecanoic acid, methyl ester	0.58	11.52	Dodecanoic acid, methyl ester	0.91
14.67	Oleic acid, methyl ester	22.0	12.70	Tetradecanoic acid, methyl ester	2.53
14.76	Stearic acid, methyl ester	9.71	13.05	Methyl tetradecanoic acid, methyl ester	2.81
15.66	Eicosanoic acid, methyl ester	0.65	13.10	Methyl tetradecanoic acid, methyl ester	1.26
16.50	Docosanoic acid, methyl ester	1.78	13.25	Pentadecanoic acid, methyl ester	0.83
			13.69	Palmitoleic acid, methyl ester	8.57
			13.78	Palmitic acid, methyl ester	17.91
			14.69	Oleic acid, methyl ester	16.90
			14.77	Stearic acid, methyl ester	6.77
			16.52	Tetramethyl stearic acid, methyl ester	1.25

PLA – CP			PLA – MIP		
Retention time (min)	Compound	Percentage quantified area	Retention time (min)	Compound	Percentage quantified area
8.50	Benzoic acid, methyl ester	46.15	4.45	Toluene	10.92
11.68	1,3-Benzenedicarboxylic acid, dimethyl ester	16.52	5.39	Propyl cyclohexane	1.20
13.84	Palmitic acid, methyl ester	25.26	5.82	Ethyl benzene	14.86
14.82	Stearic acid, methyl ester	5.99	5.93	Xylene	1.79
15.97	Eicosane	6.08	6.24	Xylene	4.66
			6.61	Cumene	1.02

6.96	Propyl benzene	0.56
7.04	1-Ethyl, 3-Methyl benzene	0.70
7.25	1-Ethyl, 2-Methyl benzene	0.69
7.30	Octamethyl cyclotetrasiloxane	1.42
7.38	Decane	1.21
7.52	1 Methoxyethyl benzene	35.93
7.96	1 Propynyl benzene	2.01
8.19	1-Phenyl Ethanone	0.92
8.27	1-Undecene	0.71
8.33	Undecane	1.44
8.41	Benzoic acid, methyl ester	2.00
9.11	1-Dodecene	0.49
9.17	Dodecane	0.66
9.25	Naphthalene	7.02
9.93	Tridecane	0.55
10.14	1-Methyl Naphthalene	0.50
10.27	2-Methyl Naphthalene	0.53
10.73	Biphenyl	1.31
11.52	1,4 - Benzenedicarboxylic acid, dimethyl ester	1.72
13.06	1-Octadecene	0.59
13.38	Phenanthrene	0.45
13.60	1-Nonadecene	0.45
13.78	Palmitic acid, methyl ester	1.47
14.67	9-Octadecenoic acid, methyl ester	1.28
14.77	Stearic acid, methyl ester	0.51
15.06	1-Docosene	0.44

STR – CP			STR – MIP		
Retention time (min)	Compound	Percentage quantified area	Retention time (min)	Compound	Percentage quantified area
3.80	Butanoic acid, methyl ester	1.67	5.07	Trimethoxyethane	8.24
4.97	Dimethoxy-2-propanone	4.82	7.41	Levulinic acid-methyl ester	6.63
5.12	Trimethoxyethane	48.33	8.30	3-Ethyl, 2-Hydroxy, 2-Cyclopentenone	5.74
5.59	Dimethoxyacetone	15.05	9.29	Naphthalene	14.95
6.13	Dimethoxy-tetrahydrofuran	1.34	10.55	2,6-Dimethoxy-phenol	6.33
6.30	Dimethoxy-2-propanone	5.37	12.72	Tetradecanoic acid, methyl ester	6.92
6.69	Tetramethoxy ethane	1.71	13.81	Palmitic acid, methyl ester	29.54
6.96	Dimethoxy propanoic acid, methyl ester	2.21	14.69	Linoleic acid, methyl ester	17.60
7.42	Levulinic acid-methyl ester	5.38	14.79	Stearic acid, methyl ester	4.04
7.60	2-Propenyl ester butanoic acid	2.02			
8.30	3-Ethyl, 2-Hydroxy, 2-Cyclopentenone	5.39			
8.42	2-Methy, 2-Butenedioic acid, dimethyl ester	1.56			
8.76	Pentanedioic adic, dimethyl ester	3.12			
10.55	2,6-Dimethoxy-phenol	2.06			