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1 **Pyrolysis and combustion of municipal solid wastes: Evaluation of synergistic effects using**

2 **TGA-MS**

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14 **Abstract**

15 A thermogravimetric methodology was developed to investigate and semi-quantify the extent of
16 synergistic effects during pyrolysis and combustion of municipal solid waste (MSW). Results
17 from TGA-MS were used to compare the pyrolysis and combustion characteristics of single
18 municipal solid waste components (polyvinyl chloride (PVC), polypropylene (PP), polystyrene
19 (PS), branches (BR), leaves (LV), grass (GR), packaging paper (PK), hygienic paper (HP) and
20 cardboard (CB)) and a mixture (MX) of PP, BR and CB. Samples were heated under dynamic
21 conditions at 20°C/min from 25°C to 1000°C with the continuous record of their main evolved
22 fragments. Synergistic effects were evaluated by comparing experimental and calculated weight
23 losses and relative areas of MS peaks. Pyrolysis of the mixture happened in two stages, with the

24 release of H₂, CH₄, H₂O CO and CO₂ between 200-415°C and the release of CH₄, C_xH_y, CO and
25 CO₂ between 415-525°C. Negative synergistic effect in the 1st stage was attributed to the
26 presence of PP where the release of hydrocarbons and CO₂ from BR and CB was inhibited,
27 whereas positive synergistic effects were observed during the 2nd degradation stage. In a second
28 part of the study, synergistic effects were related to the dependency of the effective activation
29 energy (E_{α}) versus the conversion (α). Higher E_{α} s were obtained for MX during its 1st stage of
30 pyrolysis and lower E_{α} s for the 2nd stage when compared to the individual components. On the
31 other hand, mostly positive synergistic effects were observed during the combustion of the same
32 mixture, for which lower E_{α} s were recorded.

33 Keywords: Municipal solid wastes, TGA-MS, pyrolysis, combustion, synergy

34 **1. Introduction**

35 Rapid industrialization and population growth have led to an increase in generation of municipal
36 solid wastes (MSW) to such an extent that the management of solid wastes have become a major
37 concern in developing countries [1]. In Mauritius, solid wastes were traditionally disposed off in
38 open dumps and uncontrolled landfill, which pose potential environmental threats and health
39 issues [2]. At present, the waste generation rate per capita in Mauritius is higher than most
40 developing countries [3]. Two disposal methods namely landfill and composting are currently
41 applied, although the growth in solid waste generation and the lack of landfill space requires an
42 alternative solid waste treatment [4]. On the other hand, with Mauritius being highly dependent
43 on the import of petroleum to meet its requirement of energy, the government has proposed the
44 ‘Maurice Ile Durable’ concept, aiming to be 65% self-sufficient in renewable energy by 2028. As
45 such, thermochemical techniques can be applied for the treatment of MSW because they provide

46 an efficient solution to reduce the volume of MSW, which can be subsequently converted into
47 recoverable energy as replacement for fossil fuels [5].

48 Combustion was suggested as an alternative to landfill and for the rejects of the non-compostable
49 fraction from the composting plant [4]. Combustion is the thermal processing of solid waste by
50 chemical oxidation with usually excess amount of air to produce a flue gas and a solid residue as
51 products [6]. The major combustible fractions of MSW in Mauritius are paper (12 % w/w),
52 plastic (13 % w/w) and yard waste (43 % w/w) [7]. Pyrolysis was also suggested as another
53 alternative for the treatment of MSW as it has received much attention during recent years.
54 Pyrolysis which is theoretically a zero-air indirect process for the thermal decomposition of
55 solids, presents the advantage of converting MSW into several usable products such as low
56 molecular weight gases, heavy volatiles (tar) and solid char [8,9]. The effect of heat on MSW
57 depends on the atmosphere used. The use of combustion or pyrolysis atmosphere causes different
58 types of reactions to happen and hence the degradation of solid wastes occurs by different
59 pathways producing different types of products.

60 Efficient conversion of solid wastes to energy products, through thermochemical techniques,
61 requires the understanding of their thermal behaviour [10]. Thermogravimetric analysis (TGA) is
62 a preferred technique to study the kinetic behaviour of samples' thermal degradation at low
63 heating rates although it provides limited information on products evolved and secondary
64 reactions of thermal conversion [11]. Coupling TGA with Fourier Transform Infrared
65 spectroscopy (FTIR) or with Mass Spectroscopy (MS) provides some information on the thermal
66 decomposition and reaction mechanisms. For example, Singh *et al.* [12] assessed the volatile
67 species evolved during the pyrolysis of several natural and synthetic polymers using both TGA-

68 FTIR and TGA-MS techniques and concluded that both techniques were capable of providing
69 qualitative information on the volatile species evolved during pyrolysis.

70 Several researchers have applied TGA to study the pyrolytic [5,8,13] and combustive [14,15]
71 characteristics of MSW, using selected individual waste components and/or mixtures. Previous
72 studies have shown that the pyrolysis and combustion degradation stages of various biomass
73 fuels and selected mixtures thereof were different [10, 16]. Under inert atmosphere, each
74 material degraded in a single stage, depending on the content and composition of inorganics,
75 while between two and three degradation stages were observed for each component under
76 combustion conditions. In addition, thermal decomposition processes occur at lower
77 temperatures in oxidising atmospheres as compared to pyrolysis conditions. However, there are
78 few comparative studies on the volatiles evolved from the components of MSW during
79 combustion and pyrolysis [12, 17, 18].

80 MSW is a complex mixture of different types of components. During pyrolysis and combustion
81 of MSW, the different components do not degrade independently in the mixture and some
82 interactions may give rise to synergies. Synergy occurring during co-pyrolysis and co-
83 combustion is the difference between the actual experimental yield or composition of the
84 products and the value calculated according to the ratio of the individual components in the
85 mixture [19]. Several researchers mentioned that the mechanism of synergistic effect between
86 plastic and biomass is still unclear [20, 21]. Besides, while many works describe the thermal
87 behaviour of single feedstocks, few have attempted to describe the apparent activation energy of
88 potential reactional synergies occurring during the thermal conversion of a mixture [22].

89 Therefore, the aim of this work is to study both pyrolysis and combustion of typical municipal
90 wastes to gain knowledge on eventual synergistic mechanisms. To do this, we used the TGA-MS

91 technique and determine activation energies to quantitatively describe the extent of synergetic
92 mechanisms and associated threshold..

93 **2. Materials and methods**

94 *2.1 Materials*

95 Combustible fractions from municipal solid wastes (MSW) were selected as feedstocks. In total,
96 nine different feedstocks were classified in three main categories: plastics [polyvinyl chloride
97 (PVC), polypropylene (PP), polystyrene (PS)], paper wastes [cardboard (CB), hygienic paper
98 (HP), packaging paper (PK)], and yard wastes [pine wood branches (BR), leaves (LV) and grass
99 (GR)]. A mixture (MX) between polypropylene, cardboard and branches at a mass ratio 1:1:1
100 was also prepared. Feedstocks were cut down into small pieces using a Rockwell mill and a
101 chipper for PVC and branches and milled to a 2 mm particle size using a cryogenic grinder
102 (Retsch SM 100).

103 A representative sample of each material was obtained using the standard method of coning and
104 quartering (SABS method). The particle size distribution was determined using a Retsch sieve
105 shaker operating for 10 minutes. Samples of particle size between 250 μm and 1 mm were used
106 in the TGA experiments.

107 *2.2 Analyses*

108 Proximate analysis of feedstocks was carried out in accordance to the ASTM E1131 by means of
109 a Mettler Toledo TGA/DSC1 thermogravimetric analyser. Samples were loaded in 900 μL
110 alumina crucibles and were heated under a N_2 (99.999% Baseline 5.0, Afrox) flow of 80 mL/min
111 at a heating rate of 50°C/min from 30°C to 110°C, following which an isothermal region was
112 maintained for 30 s. The heating rate was then increased to 100°C/min until a temperature of

113 900°C was reached after which a second isothermal region was hold for 5 minutes. Finally, the
114 atmosphere was changed from N₂ to O₂ (99.998% Baseline 4.8, Afrox), which flow rate was 80
115 mL/min for a further 5 minutes, to allow for complete combustion and determination of the ash
116 content.

117 Ultimate analysis was carried out using a LECO TruSpec Micro Elemental Analyser where the
118 amount of elemental carbon, hydrogen, nitrogen and sulphur present in each component was
119 determined. The oxygen was calculated by difference. The higher heating value (HHV) of the
120 feedstock was determined by means of an Eco cal2K bomb calorimeter. However, no calorific
121 value could be obtained for PVC as the release of large amount of hydrochloric acid during its
122 combustion is potentially corrosive. The results are presented in Table 1.

123 *2.3 TGA-MS experiments*

124 The thermal decomposition of individual components in MSW and their mixture was carried out
125 in a Mettler Toledo TGA/DSC 1 analyser. Each sample (10-20 mg) was placed in a 70 µL
126 alumina crucible and placed into the furnace where it was heated from 25°C to 1000°C at heating
127 rate 20°C/min. The mass used varied between the samples since their densities were different.
128 Low sample masses and low heating rate were chosen so as to reduce the occurrence of
129 secondary vapour solid interactions and the effect of mass and heat transfer [23]. Blank runs
130 were carried out to determine the effect of buoyancy on the experiments following which the
131 TGA curves were corrected. Pyrolysis and combustion experiments were carried out using
132 Argon (99.999% baseline 5.0, Afrox) and air (21% O₂/79%N₂, Afrox) respectively, at a flow rate
133 50 mL/min, with a hold time of 5 minutes before the start of the reaction, to ensure identical
134 temperature distributions and thermal equilibrium of the samples at the start of the experiments.
135 Weight loss measurements of the samples were recorded every 0.7 seconds. TGA experiments

136 were carried out in duplicate to confirm the reproducibility of the results. Data obtained from the
137 TGA were interpreted and manipulated using the STARe-Evaluation software version 13.0
138 supplied by AKTS.

139 Volatile products were analysed by a mass spectrometry (MS) coupled to the TGA. A
140 representative portion of the evolved gas components from the TG analyser was fed to a Pfeiffer
141 Vacuum ThermoStar GSD320 Gas Analysis System mass spectrometer through a well insulated
142 5m x 150 μ m fused silica capillary heated to 200 $^{\circ}$ C. The input gas was ionised by a bombardment
143 of electrons under positive electron impact ionization energy of 70eV. Cations were separated by
144 a quadrupole mass filter and reached a SEM MS detector. The subsequent mass spectrum provides
145 a fingerprint of the complex vapours. Preliminary sensitivity and linearity tests using CaCO₃
146 standard were carried out to avoid any saturation of the detector and confirming the position of
147 the capillary at the furnace exit.

148 In order to select the relevant molecular ions to track during the degradation, a preliminary-MS
149 scan of the overall volatiles was applied to screen all ionic species in the range of 1 to 300 amu
150 emitted by each sample recorded over 42 cycles. After comparison of the scans with literature
151 [12, 18, 24] a list of 8 common fragments of the most intense ($I > 10^{-12}$ A) fragments
152 (Supplementary data S1) were chosen. The intensity of the signal was normalised to the sample
153 size and to the carrier gas ion (m/z 40) in order to have a comparable ion current across different
154 stages and between different samples and to eliminate systematic instrumental errors.

155 The sensitivity and linearity of the MS detector was checked by pyrolyzing four different sample
156 weights of PVC (5, 10, 15 and 20 mg) under dynamic regime at 20 $^{\circ}$ C/min with a flow of 50
157 mL/min of Argon (99.999% baseline 5.0, Afrox). The plot of ion peak areas versus the initial
158 masses of PVC introduced (Supplementary data S2) displayed a linear trend ($R^2 = 0.9884$)

159 indicating that the MS was sensitive enough with low sample masses and that a direct
160 relationship between the peak area and the sample mass could be used.
161 The effective activation energy as a function of conversion was evaluated for the samples and
162 mixture using the popular isoconversional analysis, Friedman's method. The samples were
163 heated from 25 to 1000°C using four heating rates (10, 20, 30 and 50°C/min) under both
164 pyrolysis and combustion conditions as described above. Although these heating rates appear to
165 be too high according ICTAC kinetics committee recommendations [25] to insure the kinetic
166 regime, the main objective of this study was to demonstrate that the TGA-MS method is an
167 adequate technique to semi-quantify synergistic events during the devolatilization of complex
168 polymers by combining devolatilization rates ($d\alpha/dt$) and relative areas of MS peaks. All
169 resulting weight loss using TGA and their corresponding rate obtained from DTG curves at
170 different temperatures were treated using the Advanced Thermal Kinetics Software (AKTS
171 version 3.18). The E_α -dependency curves versus the extent of conversion were obtained using the
172 Friedman's method as described in detail by Aboyade *et al.* [26]. The equation used for the
173 determination of the apparent activation energy is given as:

$$174 \quad \ln(\beta(d\alpha/dt)) = \ln[A \cdot f(\alpha)] - E/RT \quad (1)$$

175 Where α is the conversion fraction, β is the heating rate, $f(\alpha)$ is the reaction model, A is the
176 Arrhenius pre-exponential factor and E the activation energy. A plot of $\ln(\beta(d\alpha/dt))$ against $1/T$
177 for values obtained for different heating rates (β) at the same conversion (α) results in lines. The
178 E_α -dependency analysis has been proven to be a powerful tool to describe key features of thermal
179 conversions [27].

180 **3. Results and Discussion**

181 *3.1 Weight loss profiles of MSW during pyrolysis and combustion*

182 3.1.1 For individual materials

183 Each material was exposed to inert and oxidative thermal treatments and the main degradation
184 stages are illustrated in Figures 1 and 2. Tables 2 and 3 summarise the main characteristics of
185 TGA and DTG curves such as the temperature range in which the degradation took place, the
186 temperature at which the maximal rate of loss weight occurred and the final percentage of solid
187 residue. All materials except PVC and PK were pyrolysed in one stage (Figure 1). The pyrolysis
188 degradation of PVC occurred in two distinct steps with peaks observed at 309°C and 450°C on
189 the DTG curve which are in line with previous research on the pyrolytic behaviour of PVC [28].
190 The other two plastics PP and PS decomposed in a narrow range of temperature (Figure 1 and
191 Table 2). Both plastics containing a high VM content (Table 1) presented similar pyrolysis trends
192 with the fastest rates of weight loss (Table 2). This single stage degradation can be explained by
193 the very homogeneous structure of plastics as mentioned by Bockhorn *et al.* [29]; with PP and
194 PS's degradation occurring through the same radical chain mechanism, initiating via random
195 scission followed by radical transfer. Hence the difference in the TG curves of PVC and the
196 other two plastics can be attributed to the different macromolecular structure and pyrolysis
197 mechanisms. The remaining solid residue for plastics (Table 2), as indicated by the presence of
198 ash content (Table 1) is mainly due to the presence of additives, with fibre glass being the most
199 common [30].

200 In the case of yard and paper wastes, the weight loss occurring below 100 °C is attributed to the
201 loss of moisture [31]. Subsequent to dehydration, the degradation of the components in
202 lignocelluloses (BR, LV, GR) with the lowest thermal stability started at the lowest temperatures,
203 which corresponded to the typical degradation temperature range of hemicelluloses (160-360°C)
204 [32]. Cellulosic-based (CB, HP) wastes started to degrade at a slightly higher temperature (210-

205 230°C), which corresponded to the reported temperature range of cellulose degradation (i.e., 240-
206 390°C) [32]. The lignocellulosic-based (BR, LV, GR) materials presented broader degradation
207 range (Figure 1) which was characteristic of the decomposition of lignin reported over a wide
208 temperature range (180-900°C) [32] and to their higher FC content (Table 1). Brebu and Vasile
209 [33], further attributed the broad temperature range for the thermal degradation of lignin to
210 differences in thermal stabilities of the various oxygenated functional groups present in lignin. A
211 change in the slope above 500°C for the lignocellulosic-based (BR, LV, GR) materials shows a
212 slower rate of weight loss (Table 2), corresponding to a combination of the end of cellulose
213 degradation and the start of secondary degradation of heavier volatiles and char formation
214 process [31]. The latter restricts the mass transport at the solid/gas interface and hence slows
215 down the rate of escape of the volatilized gases [31]. On the other hand, PK paper's degradation
216 pathway differed from the other cellulosic-based materials with two distinct peaks observed on
217 the DTG curve at 362°C and 486°C, respectively. A small shoulder peak was also observed at
218 690°C. Similarly to HP and CB, the first stage of degradation between 250°C and 400°C
219 corresponded to the degradation of cellulose. Skreiberg et al. [10] reported that the second stage
220 (400-510°C) was a result of the degradation of CaCO₃ to CaO and CO₂. Calcium carbonate is
221 often used as additives in these types of paper. A further thermal degradation above 500°C
222 indicated the existence of more stable molecules or intermediates, inert below this temperature.
223 Analyzing the width of the temperature range in which pyrolysis takes place for the different
224 samples, it can be seen that the 9 MSW components can be put into the following order: PS, PP,
225 BR, LV, PVC, HP, CB, GR and finally PK. PP, PS and BR had completed their thermal
226 degradation by 500°C. The first three components are also the materials with the lowest ash
227 content (Table 1). PK and GR, containing the highest ash content, continued to lose weight

228 above 600°C and were the most difficult to break down. The lower DTG peak observed for
229 grasses was also reported in other studies [13] and was explained by the higher ash content of
230 GR (Table 1) and the difference in the composition of ash.

231 The TGA and DTG curves of the combustion of the different components are presented in Figure
232 2. The DTG curves for all lignocellulosic-based materials (BR, LV, GR) were practically
233 identical (Figure 2). The first degradation stage was in the range of 200-380°C and could be
234 attributed to the breakdown of hemicelluloses and cellulose [32] up to 300°C. The second
235 combustion-degradation stage (370-550°C), which was not clearly observed during pyrolysis,
236 corresponded to the degradation of lignin although most probably due to the oxidation of char
237 [34]. In most cases, the combustion of the feedstocks occurred at lower temperatures than
238 pyrolysis (Table 3 and Supplementary data S3 for direct comparison of DTG curves). In
239 particular for the lignocellulosic-based (BR and LV) and cellulosic based (CB, HP, PK)
240 feedstocks, the rate of combustion (Table 3) was faster than the rate of pyrolysis (Table 2) at one
241 exception for the grass, which displayed the lowest O content but also the highest ash content
242 (Table 1). An increase in the content of oxygen and fixed carbon was thus beneficial to the rate
243 of combustion. These oxidation conditions also facilitated the devolatilization of inorganics for
244 all of the individual components considered, resulting in a lower weight fraction of residual
245 solids after processing (Table 3). Furthermore, the combustion of lignocellulosic-based materials
246 presents more stages of degradation than their pyrolysis degradation (Supplementary data S3).

247 Similarly to pyrolysis, the combustion of plastic materials, PP and PS, occurred in a single stage
248 but at lower temperatures (260-425°C). The absence of the second combustion stage indicated
249 that no char was formed during the first stage of combustion, since these two plastics had a high
250 VM content (Table 1). In the case of the combustion of PVC, a three staged degradation was

251 observed indicating the formation of char and its combustion in the last stage at high temperature
252 of 610°C (Figure 2). Once again, the cellulosic-based material PK presented three-stage
253 degradation under oxidative atmosphere. After a first volatilization at 335°C and the combined
254 combustion of lignin and char (425°C), a third stage at 672°C was observed and could be
255 attributed to the decomposition of calcium carbonate to calcium oxide and carbon dioxide [10].

256 3.1.2 For the mixture

257 The mixture consisted of one material from each feedstock group (i.e., lignocellulosic, cellulosic
258 and plastic-based materials), PP, CB and BR. This preparation was subjected to pyrolysis and
259 combustion under 20°C/min and main results are summarized in Figure 3. Under pyrolysis, the
260 mixture was devolatilized in two distinct stages centred at 375 and 481°C (Table 2), with the
261 former peak attributed to both devolatilization of hemicelluloses and cellulose fractions from
262 lignocellulosic and cellulosic-based materials, while the latter mainly to PP devolatilization with
263 minor contributions of lignin degradation, present in CB and BR (Table 2). Similar observations
264 were made during the thermal degradation of MSW under inert conditions, which were attributed
265 to the successive contributions of primary decomposition and secondary reactions [35].

266 Two stages of decomposition were detected during combustion (Figure 3) of the mixture. The
267 two combustion stages overlapped to a greater extent when compared to the DTG curve of
268 pyrolysis. Larger extents of volatile release, occurring at lower temperatures, were observed for
269 combustion of the mixture, compared to pyrolysis (Tables 2 and 3), as was also observed with
270 combustion/pyrolysis of single components. Significant weight loss of 88% was observed during
271 the first combustion stage (225-400°C), associated with the decomposition of all the three
272 components in the mixture (Table 3). A relatively weak and narrow peak (425°C) was observed
273 in the second stage corresponding mostly to the oxidation of char and slow degradation of lignin.

274 The rate of devolatilization for the first peak was higher during combustion while the second
275 peak was higher during pyrolysis.

276 *3.1.3 Analysis of synergistic interactions during MSW mixture pyrolysis and combustion*

277 The degradation of lignocellulosic-based and plastic materials occur through different types of
278 mechanisms which can give rise to synergies. Usually lignocellulosic-based materials degrade
279 through a series of different endothermic and exothermic reactions involving ionic/non-ionic
280 reactions [36] while plastic degradation has been reported to occur through radical mechanism.
281 In order to investigate the synergistic behaviour between the lignocellulosic-based and plastic
282 materials in the mixture, theoretical DTG curves were also calculated as the sum of the weight
283 loss rate contributions from BR, CB and PP fractions obtained under same conditions as shown
284 in Figure 4. It was then assumed that there is no interaction between the different materials
285 within the mixture. The predicted DTG curve was obtained using an additive equation (2):

$$286 \quad Y = (x_c Y_c + x_b Y_b + x_p Y_p)/100 \quad (2)$$

287 where Y refers to the predicted weight loss rate for the blended sample, Y_b is the observed
288 weight loss rate at 100% BR, x_b is the fraction (%) of BR in the blend sample, Y_c is the observed
289 weight loss rate at 100% CB, x_c is the fraction (%) of CB in the blend sample, Y_p is the observed
290 weight loss rate at 100% PP and x_p is the fraction (%) of PP in the blend sample.

291 Under pyrolytic conditions, from the first peak at 375°C, the reaction is slower than the
292 calculated results showing some interactions between BR and CB, which is known to decompose
293 in this temperature range. A slight shift of the second peak to higher temperatures could be
294 observed. Synergistic effects were more evident for combustion of MX. The two expected peaks
295 at 340°C (BR and CB) and 380°C (PP) have merged to produce one single peak at 348°C. The

296 synergistic behaviour for the mixture under combustion conditions occurred over the temperature
297 range from 260°C to 515°C.

298 To further discuss on the extent of the synergistic effect during the pyrolysis and combustion of
299 the mixture, the difference of weight loss, ΔW (%), was calculated using equation (3).

$$300 \quad \Delta W = W_{mix} - (x_b W_b + x_c W_c + x_p W_p) \quad (3)$$

301 Where W_{mix} is the experimental value from the TG curve of the mixture and W_b , W_c and W_p are
302 the weight losses from the TG curves of 100% BR, CB and PP. Figure 5 shows the plots of the
303 synergistic effects for the pyrolysis and combustion of MX. Negative values show a synergistic
304 effect towards the formation of char while positive values indicate synergistic effect during co-
305 pyrolysis and co-combustion for the formation of volatiles. For pyrolytic degradation, in the
306 temperature range of 25-330°C, a positive deviation of around 1.5% was observed indicating that
307 a minimum interaction between CB and BR occurred with a slightly higher release of volatiles
308 than expected. Between 330-500°C, two peaks can be observed on the curve that can be related
309 to negative synergistic effects. The first peak at 400°C, corresponding to the beginning of the
310 thermal degradation of PP, indicated that reactions between pyrolysis intermediates evolved from
311 the decomposition of the mixture led to the formation of more thermally stable compounds than
312 in the case of the single feedstock. At this temperature, the main degradation zone for PP, BR
313 and CB overlaps. The presence of intermediate species evolved during the degradation of BR
314 and CB could affect the degradation of PP by abstracting free hydrogen produced during
315 pyrolysis (Hydrogen transfer effect). Therefore the first negative synergistic peak observed is
316 most probably due to the abstraction of hydrogen by reactive species (e.g., radicals) which are
317 not available anymore to participate further in depolymerisation reactions. The second peak, with
318 a maximum of -4% at 480°C is coincident with the DTG peak temperature of degradation of PP

319 (Table 2). The volatile matter content of PP (Table 1) is much greater than that of BR and CB. At
320 this temperature (480°C), during the degradation of MX, a large quantity and wide variety of
321 volatiles was released from PP in a very short time period (Figure 6). Some of the volatiles may
322 have been trapped in the particles' voids or condensed on BR, CB and PP particles' surface
323 preventing the volatiles to be released. Further increase in temperature (>500°C) resulting in an
324 inner pressure of the particles of BR, CB and PP was then beneficial for the formation and
325 release of volatiles. Also, the negative synergistic effect due to the abstraction of hydrogens
326 reported earlier at lower temperature is reduced since the degradation of PP should be completed
327 by 500°C (Table 2). Positive deviation of around 3% was therefore observed and consistent over
328 the whole conversion suggesting that interactions between reactive volatiles and/or between
329 volatiles/solid promoted devolatilization reactions or inhibited reactions such as re-condensation
330 and char formation. Past work on co-pyrolysis of plastic and biomass suggested that the
331 formation of reactive radicals from PP could have catalyzed the decomposition of lignin
332 producing more volatiles than expected towards the end of the degradation [37]. To further
333 analyse the extent of synergistic effect, the root mean square (RMS) value was used. This
334 method used in previous research allows the determination of the error between the measured
335 and predicted values [22]. The RMS value of the deviation between the measured and calculated
336 value was 2.38 which suggest that there were indeed synergistic effects during the co-pyrolysis
337 of BR, CB and PP resulting in an overall less residual char.

338 During combustion, no difference in weight loss was observed ($\Delta W < 0.6\%$) below 250°C. In the
339 temperature range of 260-500°C, large and positive deviations in weight loss was obtained with
340 two peaks occurring at 340 and 370°C. The first synergistic peak with a maximum of 9.2%, was
341 coincident to the peak DTG for both degradations of BR and CB (Table 3) and the early stage of

342 PP degradation, which indicates that significant synergistic mechanisms promoting the
343 devolatilization of solid occurred. Contrary to pyrolysis, the formation of free hydrogen radicals
344 from PP is significantly reduced in the presence of oxygen. Therefore positive deviations
345 observed could be related to the formation of steam, which could promote the further cracking of
346 char from BR and CB leading to the formation of more volatiles. The second peak with a
347 maximum of 14%, occurred at the critical temperature where PP degraded (Table 3) together
348 with the second stage of degradation of individual lignocellulosic components, BR and CB.
349 Radicals formed during the degradation of PP contributed to the formation of volatiles from BR
350 and CB; thus suggesting that the nature of volatiles produced under oxidative atmosphere is more
351 reactive. Above 500°C, negligible and positive deviations ($\Delta W < 1\%$) were depicted (Figure 5). A
352 RMS value of 3.37 for the ΔW was obtained which was higher than that obtained during
353 pyrolysis. The RMS values indicated that the consequences related to the synergistic effects
354 during the co-thermal conversion of BR, CB and PP yielded to smaller solid residue.

355 *3.2 Evolved gas analysis during MSW pyrolysis and combustion*

356 *3.2.1 For individual materials – common fragments*

357 The composition of gaseous products from the pyrolysis and combustion of individual
358 components were analysed by online MS coupled to TGA. Figures 6 and 7 show the evolution of
359 the six common fragments under pyrolytic and combustive conditions respectively. The
360 structural formula of PVC, PP and PS are $-\text{[CH}_2\text{-CHCL]}_n-$, $-\text{[CH}_2\text{-CHCH}_3\text{]}_n-$ and $-\text{[CH}_2\text{-}$
361 $\text{CHC}_6\text{H}_5\text{]}_n-$ respectively. Since no oxygen is present in the structure of these materials, in theory
362 it suggests that H_2O , CO and CO_2 should be absent in gaseous products obtained from their
363 pyrolysis. Hence, the evolution profiles of H_2O , CO and CO_2 for PVC, PP and PS were not
364 considered in Figure 6(a, b and c). When comparing the relative abundance of some selected

365 molecular ions (i.e. H_2 , CH_4 , H_2O , C_xH_y , CO and CO_2) common to all feedstocks, H_2 , CH_4 and
366 other hydrocarbons (HCs) were found to be released more abundantly under pyrolysis
367 conditions, while H_2O , CO and CO_2 presented the highest intensities during combustion.

368 *H₂O in gaseous products*

369 H_2O release characterized by molecular ion fragment 18 amu, was released at several stages
370 during the pyrolysis of natural polymers. Figures 6d-h revealed the presence of two peaks for
371 H_2O during the thermal degradation of yard and paper wastes. The first peak below $200^\circ C$ can be
372 related to the first peak observed on the DTG curves of ligno-cellulosic based materials (Figure
373 1b) which corresponded to the release of moisture. The second peak, which occurred in the
374 thermal degradation range of cellulose, was more pronounced for paper wastes (CB, HP and PK)
375 and attributed to their higher cellulosic content when compared to those of yard wastes. The peak
376 observed in the pyrolysis stage can be mainly ascribed to the release of intra molecules of water
377 [9] from the hydroxyl group present in the structure of cellulose and to the release of hydroxyl
378 groups during the degradation of higher molecular weight molecules [38].

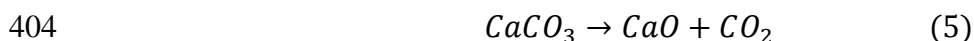
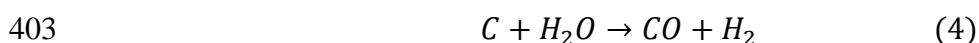
379 Under combustive conditions, the recurrent record of higher intensities of H_2O^+ ions for PP and
380 PS indicated that the oxidation of HCs present in plastic is an important mechanistic feature. PP
381 displayed the highest intensity for the release of H_2O during combustion which is consistent with
382 the high hydrogen content of PP (Table 1). The three MS peaks of H_2O observed during the
383 combustion of PVC were found in good agreement with its DTG profile (Figure 2b). The release
384 of H_2O during combustion of lignocellulosic-based materials (BR, LV, GR, CB, HP and PK)
385 occurred in two main steps. Similarly to pyrolysis, the release of water at low temperature could
386 correspond to dehydration. The second peak of H_2O may be attributed to the degradation of

387 glycosyl units present in cellulose [39] and most probably due to the oxidation of HC's released
388 in that temperature range (200-500°C).

389 *CO₂/CO in gaseous products*

390 During pyrolysis, the non-condensable, CO (m/z 28) and CO₂ (m/z 44), evolved over the whole
391 temperature range up to 600°C (Figures 6d-h). Higher proportions of CO₂ during the degradation
392 of lignocellulosic-materials (BR, LV, GR) were detected while more CO was released during the
393 degradation of cellulosic-based materials (CB, HP, PK). The formation of CO₂ is believed to be a
394 consequence of the degradation of carbonyl (C=O) and carboxyl groups (COOH) present in
395 hemicelluloses and cellulose and the product CO is the result of the scission of ether bonds (R-O-
396 R') [40] indicating that ether groups are more dominant in paper wastes than yard wastes. At
397 higher pyrolysis temperatures (>600°C), peaks of CO and CO₂ could be observed for paper
398 wastes suggesting self-gasification according to equation (4) [18] and also the decomposition of
399 calcium carbonates (equation (5)) present in paper wastes [41].

400 Stronger magnitude of both ions signal was observed for all the waste components burnt. Highest
401 peaks were exhibited by PP and PS at 340°C and 420°C, respectively as the rich carbon content
402 of the plastics (Table 1) were oxidised to CO and CO₂ in presence of air.



405 *H₂ in gaseous products*

406 It is widely accepted that H₂ is mainly produced from the cracking of HCs and their subsequent
407 degradation. Figure 6 revealed the presence of H₂ from the pyrolytic degradation of all the nine
408 components. At higher temperatures (600-1000°C), the concentration of H₂ increased
409 considerably for PVC, yard and paper wastes during pyrolysis. Similar observations were made

410 for CO (m/z 28) where H₂ is being produced following equation (4). Secondary cracking of
411 higher molecular weight compounds and secondary pyrolysis of char residue contributed to the
412 release of H₂ at elevated temperatures. The change in atmosphere from argon to air caused a high
413 decrease in the intensity of H₂⁺ ions, which could be attributed to the formation of water.
414 Compared to the signals of the other light gases (CO, CO₂ and H₂O), the signal for H₂ was
415 considered negligible in Figure 7.

416 *C_xH_y in gaseous products*

417 The fragment ions of m/z 16 (CH₄⁺) and m/z 26 (C₂H₂⁺) are mainly representative of the
418 evolution of HCs. The intensity of the fragments for CH₄ was higher in most cases showing the
419 cracking and evolution of lighter molecular gases. A single narrow peak for both fragments
420 could be observed for PP and PS in the degradation stage at around 480 °C. Higher concentrations
421 in ions were observed in the second stage of devolatilization of PVC as HCs are formed after the
422 elimination of chlorine in the first stage and were subsequently degraded at higher temperatures
423 during the second stage. For cellulosic-based materials (BR, LV, GR, CB HP and PK), the first
424 peak shows the production of CH₄ mainly comes from the cracking of methyl and methylene
425 groups present in hemicelluloses and cellulose and the second peak originates from the
426 degradation of lignin.

427 In the presence of oxygen, HCs were oxidised to H₂O and CO₂ causing a significant decrease in
428 the intensity of m/z 16 and m/z 26 (Figure 7). The intensity of m/z 16 was however higher than
429 expected and attributed to the amount of O₂ in air.

430 *HCN/NH₃ in gaseous products*

431 The evolution of m/z 16 and m/z 26 are affected by the presence of NH₃ and HCN, respectively
432 [24]. However, volatile nitrogenous gaseous compounds such as HCN and NH₃, are known to be

433 present in significantly low concentrations in waste materials [42, 43]. The nitrogen content of
434 the different components in this study varied between 0 to 3% (Table 1), with plastic wastes
435 having negligible nitrogen content and GR having the highest. Giuntoli et al. [44] detected low
436 amounts of NH₃ and HCN compared to the levels of other volatile species during the pyrolysis of
437 biomass residues. The gas analysis in another study [35] did not reveal the presence of NH₃ and
438 HCN. To conclude, the peaks at m/z 16 and m/z 26 could be associated to the simultaneous
439 release of NH₃ and HCN and mainly HCs in the case of cellulosic-based components; thus
440 illustrating some limitations in the use of hard ionization source with mass spectrometry.
441 Higher intensity of signals attributed to H₂, CH₄ and HCs and lower intensity for CO, CO₂ and
442 H₂O signals collected under pyrolytic conditions suggest that the gas released could have a
443 higher specific energy than combustion gas.

444 *3.2.2 For the mixture of PP, BR and CB*

445 For the sake of comparison, the MS peak areas were normalized to the initial mass of each
446 feedstock to better illustrate synergistic effect when mixing PP, BR and CB. Also, a calculated
447 MS peak area for the mixture, MX_{calc}, was determined by summing the relative contribution of
448 each single component (Table 4). The MS curve of the different fragments for MX under
449 pyrolytic and combustive conditions is given in Figure 8.

450 *H₂O in gaseous product of the mixture*

451 Water (m/z 18) evolution up to 200°C was observed during both degradation conditions and was
452 due to the free and physically bounded water in CB and BR. The relative area of the first peak
453 for both combustion and pyrolysis was 0.06nsA/mg and was close to the relative area obtained
454 from CB (0.063nsA/mg) and BR (0.020nsA/mg). A second peak was observed at around 380°C
455 during pyrolytic degradation which corresponded mostly to the degradation of CB and BR. Both

456 calculated and experimental normalized areas, 0.0320 and 0.0328 nsA/mg respectively, were
457 found close; thus suggesting that external water did not participate to further chemical reactions.
458 Peaks of H₂O were absent during the second stage of degradation where mostly the
459 devolatilization of PP takes place.

460 With respect to the combustion of MX, a second peak at 370°C displayed an experimental
461 normalized area, 0.19 nsA/mg, slightly higher than the calculated value, 0.15 nsA/mg. In this
462 temperature range, positive deviations were observed (Figure 5) for the decomposition of MX
463 suggesting that synergistic effect should affect mainly secondary reactions such as the secondary
464 cracking of the char and oxidation of hydrocarbons. Hence a higher release of H₂O fragments
465 was observed.

466 *CO₂/CO in gaseous products of the mixture*

467 Under pyrolysis conditions, significant releases of CO and CO₂ were observed at 375°C, 475°C
468 and 700°C. The highest peaks observed in the first stage were related to the degradation of BR
469 and CB (Figure 6). Deviations between first stage experimental and calculated normalized areas
470 (Table 4) confirmed that at this temperature (375°), the release of CO₂ and CO was inhibited.
471 This result is in accordance to ΔW (Figure 5) where negative deviations were observed in this
472 temperature range (230-400°C). It corresponds to the start of the degradation of PP where due to
473 hydrogen transfer effects, the release of volatiles was slowed down. Similarly, for the second
474 peak (475°C), lower peak areas were obtained (Table 4) which can be related to the negative
475 synergies observed at this temperature (Figure 5). The peak for the second stage corresponds to
476 the DTG peak of PP and the high release of hydrocarbons from the structure of PP prohibited the
477 release of CO and CO₂ from lignocellulosic materials. Peaks observed at higher temperatures

478 were similar to those obtained for CB and BR (Figure 6) showing self-gasification and
479 degradation of carbonates.
480 The intensity of the peaks was higher during combustion showing the oxidation of hydrocarbons
481 as compared to pyrolytic conditions. The experimental areas of the peaks were higher than the
482 contribution from each component in the sample and occurred at the temperature where high
483 positive deviations were obtained (Figure 5) showing that CO and CO₂ were important products
484 during combustion resulting from synergistic reactions.

485 *H₂ in gaseous product of the mixture*

486 The significant and gradual increase in H₂⁺ ions observed for MX pyrolysis could be related to
487 the cracking of heavy hydrocarbons also known as secondary reactions. An opposite trend was
488 observed during combustion where the concentration of H₂⁺ ions decreased constantly.

489 *C_xH_y in gaseous product of the mixture*

490 During pyrolysis of MX, 2 peaks were observed for m/z 16 (CH₄⁺) and m/z 26 (C₂H₂⁺) at about
491 380 and 500°C. The normalized area of the first peak was lower than the calculated area
492 suggesting that the presence of PP inhibited the release of the volatile hydrocarbons from BR and
493 CB as also observed as a negative synergistic effect at this temperature (Figure 5). The second
494 peak displayed a larger area than expected (Table 4) confirming the high reactivity of PP's
495 intermediates at higher temperature promoting the thermal degradation of heavy non-volatiles
496 into CH₄ and C₂H₂ ions. At this temperature, positive deviations were also observed (Figure 5)
497 which shows that the extent of devolatilization (ΔW) is in accordance to the MS peak areas.
498 It is worth noting that the release of ions during the combustion occurred in the same temperature
499 range, 250-415°C, than pyrolysis. The experimental area value of 0.0099 nsA/mg appeared to be
500 higher than the calculated one, 0.0005nsA/mg showing positive deviations.

501 *3.3 E_α-dependency analysis for overall reactions and individual stages*

502 In order to gain qualitative insights into the synergistic effects occurring during the blending of
503 MSW components, the apparent activation energy (E_α) for the overall and single stages of PP,
504 BR, CB and MX pyrolysis was determined and presented in Figure 9.

505 The E_α-dependency analysis for PP indicates that this latter remains quasi constant throughout
506 the entire pyrolysis and combustion, and therefore the single degradation stage (Figures 1 and 2)
507 can be associated to the single and averaged values of ~ 250 kJ/mol and 90 kJ/mol, respectively.

508 Although the thermal degradation of PP during pyrolysis mainly involves the breaking of the C-
509 C bonds whose energy bond is around 350 kJ/mol [27], a lower E_α was obtained for PP and can
510 therefore be attributed to the presence of weak link sites [45]. The slight variations from the
511 average value maybe related to the occurrence of various initiation mechanisms (e.g., breakage
512 of head to head linkages, fractionation of vinylidene-end groups) and random scission [46].

513 Under oxidative conditions, the lower E_α values between 75-90 kJ/mol for PP indicated that
514 oxygenated compounds may have favoured the thermal degradation pathways due to the
515 presence of hydroperoxide radicals according to Vyazovkin and Sbirrazzuoli [27].

516 As expected, pyrolysis and combustion of the biomass (BR) underwent through more complex
517 reactions mainly 2 main degradation stages. For BR pyrolysis, the initial average E_α values, 160
518 kJ/mol (Figure 9b) were found similar to those reported for the degradation of hemicelluloses,
519 107-164 kJ/mol [46]. An increase in E_α values to ~230 kJ/mol could mark the beginning of
520 cellulose decomposition, which in general varies between 200 and 230 kJ/mol [46]. In the case
521 of biomass combustion, these latter are usually associated to the devolatilization stage with
522 average E_α values decreasing from 295 kJ/mol to 95 kJ/mol and to the char oxidation stage with a
523 practically average value of around 150 kJ/mol. When considering the respective E_α-dependency

524 determined for each stage, the start of 2nd combustion stage requires less energy than the 1st
525 combustion stage. E_{α} during pyrolysis were higher than combustion showing a different
526 degradation mechanism occurring in air with reactions of lower activation energy.

527 The E_{α} during the initial degradation stage of cellulosic derived feedstock (CB) was lower than
528 that ascribed to the biomass-derived feedstock (BR) with average values of ~ 65 kJ/mol during
529 both pyrolysis and combustion. During pyrolysis of CB, an averaged E_{α} value of 200 kJ/mol was
530 obtained which corresponded to those of cellulose degradation [46]. The almost constant E_{α}
531 values (Figure 9c) confirmed the uniform energetic demand of cellulose degradation reactions.
532 For combustion, lower E_{α} of around 170 kJ/mol were obtained in the first stage of degradation as
533 compared to E_{α} of around 200 kJ/mol in the second stage. Similar to BR, E_{α} were lower during
534 combustion when compared to pyrolysis. The degradation of cellulose in air might therefore be
535 enhanced by molecular oxygens through radical interactions.

536 When the mixture was respectively exposed to inert and oxidative atmospheres (Figure 9d),
537 comparable key features in E_{α} -dependency were observed: both processes occurred in 2 main
538 stages with higher average E_{α} values for pyrolysis. However, slight deviations in E_{α} values from
539 those obtained for the single feedstocks were found. For example, the E_{α} values and the
540 noticeable decreasing trend of the E_{α} curve for the 1st degradation stage when α is increased is
541 almost equivalent to E_{α} -dependencies obtained for CB and BR. This result suggests that
542 mechanisms involved during 1st stage of MX pyrolysis are equivalent to those of cellulose-
543 derived feedstocks and can explain the absence of synergies mentioned in section 3.1.3. The
544 second stage of degradation of MX is mainly dominated by the degradation of PP. The E_{α} values
545 for the 2nd stage were higher than those for PP, BR and CB up to $\alpha=0.65$ during pyrolysis (Figure
546 9d) thus indicating that intermediate species involved have a greater thermal stability. This

547 greater amount of energy required of around 300 kJ/mol instead of 250 kJ/mol, corresponds to
548 the negative synergistic effects described earlier in the section 3.1.3 and is attributed to PP
549 degradation. However, this energy penalty is compensated by the lowest energetic requirements
550 for $\alpha > 0.7$ reaching 160 kJ/mol at $\alpha=0.9$. These lower E_a values suggest that further
551 degradations of PP eased the overall degradation mechanisms, which is in accordance with the
552 positive synergistic effects described earlier in section 3.12. This lower activation energy and
553 positive deviations were observed until the end of the second degradation stage. In the case of
554 combustion, this positive impact of PP addition was even more significant with noticeable lowest
555 E_a values for both degradation stages (Figure 9d), which was also corroborated by the extent of
556 positive synergy effects (Table 4). Less energy is required during the combustion of MX as
557 compared to the single components. Positive synergistic effects are indeed present during
558 combustion of MX where the degradation mechanism occurs through a lower activation energy
559 pathway. Similar to the single components, lower E_a was observed during combustion as
560 compared to pyrolysis and hence indicating that the presence of oxygen indeed changes the
561 degradation pathway with reaction of lower energies occurring.

562 **4. Conclusions**

563 Real time pyrolysis and combustion characteristics (i.e., solid conversion and release of
564 volatiles) of nine components representative of current waste streams found in Mauritius and
565 their mixture were investigated using a thermogravimetric analyser coupled to a mass
566 spectrometer (TGA-MS). The mixture of MSW composed of lignocellulosic and plastic-based
567 materials was degraded in two main stages under pyrolysis conditions while the combustion of
568 the same mixture occurred in one main stage. Considering the differences between experimental
569 and calculated results, it was found that both negative and positive synergistic effects were

570 present at different stages during pyrolysis. Negative synergistic effects observed in the 1st stage
571 of pyrolysis between 330-550°C associated with higher E_a resulted in the formation of solid
572 residue delaying the degradation of lignocellulosic materials. In this stage, the expected areas for
573 the release of CH₄, CO and CO₂ were lower than experimental areas obtained showing that the
574 release of the volatiles were slowed down. Above 500°C, increasing weight losses indicated that
575 the decomposition of solid residues was favoured due to the presence of heterogeneous reactions
576 of lower E_a between the char and reactive volatiles evolved from the degradation of PP. The
577 difference between the value of the expected and experimental peak areas for the different
578 volatiles tracked also confirmed the presence of positive synergies in this stage. Under oxidative
579 atmosphere, only positive deviations up to 14% were recorded between 260-500°C; thus
580 indicating that homogeneous interactions between volatiles enhanced the combustion of the
581 mixture associated with lower E_a . This study confirms that the adopted experimental
582 methodology based on TGA-MS is suitable for revealing the extent of synergistic reactions
583 during co-pyrolysis and co-combustion.

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716 **Table 1**
717 Standard fuel analysis
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Sample	Proximate Analysis (wt% db)				Ultimate Analysis (wt% db)					HHV (MJ/kg)
	MC	VM	FC	Ash	C	H	O ^a	N	S	
PVC	0.02	88.95	8.67	2.36	38.8	5.14	53.61 ^b	0.09	-	n.d
PP	0.00	99.85	0.00	0.15	85.03	14.8	0.00	0.00	0.00	42.80
PS	0.50	99.24	0.02	0.24	90.55	7.82	0.00	0.17	1.22	38.60

BR	0.71	79.80	17.27	2.22	45.35	5.96	44.55	0.22	1.70	21.43
LV	1.68	72.53	20.76	5.03	46.13	6.15	42.13	0.56	0.10	17.66
GR	1.77	61.27	14.86	22.10	32.65	4.95	35.24	3.07	1.99	20.64
CB	3.24	78.07	8.64	10.05	40.64	6.19	42.97	0.05	0.10	20.46
PK	3.40	78.38	7.43	11.79	42.6	6.41	37.08	0.21	1.91	22.75
HP	3.20	83.55	10.04	3.21	39.6	5.74	49.40	0.20	1.85	15.30

db- Dry Basis MC-Moisture content VM- Volatile matter FC-Fixed Carbon HHV- Higher Heating Value

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^aBy difference

^bIt is CI for PVC

725 **Table 2**
 726 Characteristics of the TGA experiments of single components under pyrolytic conditions
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Sample	Solid Residue at 1000°C (%)	DTG peak temperature (°C)	DTG max (1/s)	T _{onset} (°C)	Temperature Range (°C)
PVC	11.5	327, 495 ^a	-0.0032, 0.0013 ^a	- 296	240-400, 400-560
PP	2.8	479	-0.0099	454	370-500
PS	2.9	425	-0.0099	409	330-475
BR	18.7	375	-0.0025	320	201-500
LV	23.8	368	-0.0015	299	150-520
GR	25.5	330	-0.0019	274	160-600
PK	15.5	362, 486, 700 ^a	-0.0030, 0.0017, 0.0003 ^a	- 328 -	230-410, 410-540, 540-720
CB	16.7	370	-0.0039	333	230-600
HP	10.7	375	-0.0051	334	210-560
MX	9.84	375, 481	-0.02, -0.03	327	200-415, 415-525

728 ^a Several distinct peaks observed
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Table 3
Characteristics of the TGA experiments of single components under combustion conditions

Sample	Solid residue at 1000°C (%)	DTG peak temperature (°C)	DTG max (1/s)	T _{onset} (°C)	Temperature Range (°C)
PVC	0.14	309, 450 ^a	-0.0045, 0.0115 ^a	- 295	225-375, 430-500, 500-690 ^a
PP	1.19	380	-0.0058	348	260-400
PS	1.21	400	-0.0080	380	275-425
BR	1.67	335, 460 ^a	-0.0039, 0.0007 ^a	- 311	200-370, 370-520 ^a
LV	4.00	230, 430 ^a	-0.0021, 0.0014 ^a	- 291	190-370, 370-550 ^a
GR	9.85	295, 435 ^a	-0.0017, 0.0014 ^a	- 257	125-360, 360-545 ^a
PK	8.78	335, 425, 690 ^a	-0.0043, 0.0010, 0.0028 ^a	- 312 -	280-380, 385-490, 500-715
CB	10.30	340, 420 ^a	-0.0063, 0.0013 ^a	- 327	210-375, 375-480 ^a
HP	0.53	345, 435 ^a	-0.0087, 0.0036 ^a	- 328	260-385, 385-500 ^a
MX	3.45	348, 425 ^a	-0.04, -0.001	311	225-400, 400-470

^a Several distinct peaks observed

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774 **Table 4**
 775 Relative areas of MS peaks for MX and pure components

m/z	Pyrolysis									Combustion				
	Stage 1 (nsA/mg)				Degradation Stages					Stage 1 (nsA/mg)				
	BR	CB	MX _{calc}	MX _{exp}	BR	CB	PP	MX _{calc}	MX _{exp}	BR	CB	PP	MX _{calc}	MX _{exp}
16	0.0003	0.0017	0.0020	0.0010	-	-	0.0013	0.0013	0.0047	0.0030	0.0013	0.0030	0.0073	0.0096
18	0.0150	0.0170	0.0320	0.0328	-	-	-	-	-	0.0430	0.0270	0.0800	0.1500	0.1900
26	0.0003	0.0013	0.0016	0.0006	0.0001	-	0.0051	0.0052	0.0073	0.0002	0.0003	0.0027	0.0032	0.0039
28	0.0057	0.0122	0.0179	0.0153	0.0023	0.0008	-	0.0031	0.0026	0.0640	0.0770	0.0910	0.2320	0.2340
44	0.0107	0.0117	0.0224	0.0196	0.0014	-	-	0.0014	0.0007	0.0550	0.0610	0.0740	0.1900	0.2100

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