

THERMAL AND CATALYTIC DEGRADATION OF GRAPE SEEDS/POLYETHYLENE WASTE MIXTURE

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Received August 19, 2013

Thermal degradation of grape seeds alone and mixed with polyethylene was studied by TG-MSD and by pyrolysis at 500 °C, followed by GC-MSD analysis of liquid products. The maximum degradation rate was found at 390 °C for grape seeds and at 475 °C for polyethylene. Interactions are possible between the two materials or their degradation products at co-pyrolysis, with an effect on product yield. The main components of pyrolysis oils from grape seeds are fatty acids, followed by lignin-derived compounds. Light carboxylic acids, homologous series of paraffins and olefins and benzene derivatives were also identified. The effect of Red Mud and FCC catalysts on the thermal behaviour and on the pyrolysis yield was tested in liquid and vapour phase contact mode. They enhanced the degradation and changed the product yield.

Keywords: grape seeds, polyethylene, organic waste, co-pyrolysis, Red Mud, FCC, catalysts

INTRODUCTION

The utilisation of grape residue as a renewable energy resource responds to concerns over the protection of the environment and the security of energy supply. For example, over 67 million tons of wine grapes were harvested in 2005 all over the world, of which more than 20% typically becomes waste during wine production. Grape residues consist mainly of the redundant skins, stalks and seeds that remain once the juice has been extracted. This residue must be treated effectively to avoid a number of environmental hazards, ranging from surface and groundwater pollution to foul odours.

The grape residue contains a large amount of organic constituents (i.e., cellulose, hemicelluloses and lignin) and has a high-energy content. Therefore its conversion to renewable energy would be attractive since it would solve pollution problems, reduce greenhouse gas emissions and provide a clean, low sulphur fuel.

Grape seeds contain several polyphenols and antioxidants, including oligomeric proanthocyanidin complexes, which show some health benefits.^{1,2} However, cold-pressed grape seed

oil itself does not contain significant amounts of these antioxidants since proanthocyanidins are insoluble in lipids. They are present in much higher concentrations in other parts of the grape, such as grape seed extract, grape skins, and in particular red wine.

The kinetics of devolatilization was studied by thermo-gravimetry on grape seeds, skins, stalks, marc, vine-branches, grape seed oil and grape seeds depleted of their oil.³ Pyrolysis gas chromatography mass spectrometry on archaeological grape seeds demonstrated good carbohydrate preservation over the years.⁴ Activated carbon was prepared from grape seeds by one-step pyrolysis in the presence of steam to remove metal ions from water.⁵

Various thermo-chemical processes have been developed to produce biofuels from biomass.⁶ Pyrolysis allows conversion of biomass into liquid bio-oil, combustible gas and solid char. The liquid bio-oil has a higher material and energy density and is easier to transport and store than the original biomass. The pyrolysis gases can be used to provide the energy required for the

endothermic pyrolysis process. The solid char product, due to its low sulphur and phosphorus contents and to its structural and reactivity properties, is widely used in the chemical, pharmaceutical and food industries.

The pyrolysis of grape residue has been investigated under different experimental conditions.⁷ Apart from the limited bench scale, studies were carried out in packed bed reactors. However, fluidised bed reactors are the most popular configurations owing to their ease of operation and scale-up.⁸ However, the thermal sustainability has not yet been investigated for the pyrolysis process. Co-pyrolysis of biomass with polyolefins was considered as a possibility to enhance the liquid production from biomass and to decrease the oxygen content of the biomass pyrolysis oils since polymers, such as polyethylene (PE), polypropylene (PP) and polystyrene (PS), produce oils, which contain about 14 wt% hydrogen and a very low amount of

oxygen.^{9,10} Catalysts were used to improve the quality of the obtained oils.^{11,12}

In our previous works, we discussed the co-pyrolysis of mixtures such as materials from tetra pak,¹³ scrap tires with oily waste,¹⁴ pine cone and LignoBoost[®] lignin with synthetic polymers.^{15,16} Here we present the co-pyrolysis of grape seeds with polyethylene.

EXPERIMENTAL

Materials

Grape seeds (GS) as biomass waste and waste polyethylene (PE) were considered for this study. Grape seeds were supplied by Bozacada, Turkey, as dried residue remaining after juice extraction from mixed varieties of grapes in wine industry processing. The polyethylene waste was supplied by Muzaffer Pınarbaşı Company, Izmir, in the form of fluff, collected and separated from municipal waste; it was used as received. Some properties and composition of the grape seeds are given Table 1.

Table 1
Proximate, ultimate and component analyses of grape seeds

Proximate analysis (as received, wt%)	
Moisture	8.1
Volatile matter	2.9
Fixed carbon	69.5
Ash	3.3
Component analysis (dry, wt%)	
Cellulose	32.7
Hemicellulose	37.6
Lignin	24.9
Extractives	0.67
Ultimate analysis (dry, wt%)	
C	53.0
H	5.7
N	1.84
S	0.15
O ^a	39.3
Gross calorific value (MJ/kg)	20.7

^a calculated by difference

The catalytic experiments were performed over Red Mud (RM), as a disposable catalyst, and over a commercial ReUS-Y faujisite type catalyst (FCC), which is being used in the fluid catalytic cracking unit in refinery processes. Red Mud was supplied by Seydisehir Aluminium Company, Turkey, as a sludge, which was then filtered and dried at 110 °C in the laboratory. It contained mainly Fe₂O₃ – 37.72 wt%, Al₂O₃ – 17.27 wt%, SiO₂ – 17.10 wt%, TiO₂ – 4.81 wt%, Na₂O – 7.13 wt%, CaO – 4.54 wt%, and had a

specific surface area of 16 m²/g. The FCC catalyst was supplied by Turkish Petroleum Refineries Corporation, Izmir, Turkey, and had the following characteristics: SiO₂ – 58.0 wt%, Al₂O₃ – 38.0 wt%, Re₂O₃ – 1.5 wt%, Na₂O – 0.3 wt% and Fe – 0.5 wt%; density – 0.89 g/cm³; specific surface area – 255 m²/g; pore volume – 0.25 cm³/g. Both catalysts were in fine powder form. Briefly, the following abbreviations were used in this paper: GS – grape seeds; PE – polyethylene; RM – Red Mud; FCC – fluid cracking catalyst; Lpc – liquid phase

contact mode for the use of catalyst; Vpc – vapour phase contact mode for the use of catalyst.

Pyrolysis procedure

The pyrolysis experiments were performed by semi-batch operation and self-generated atmosphere in a glass reactor with an internal diameter of 30 mm and a length of 350 mm, which is schematically presented in Figure 1. The reactor was heated by 10 °C/min up to the final degradation temperature of 500 °C, which was held for 1 h.

The pyrolysis temperature in this study was selected based on the temperature of complete degradation of polyethylene found from TG data. The condensable degradation products were water-cooled in a condenser and collected in a graduated cylinder, while the gases that were non-condensable at room

temperature were passed through a flask with water and then collected in a Teflon bag.

Catalysts were used in pyrolysis and co-pyrolysis of biomass or/and plastics in two modes, namely in liquid (Lpc) or vapour (Vpc) phase contact. In Lpc mode, the catalysts were mixed with the pyrolysing materials at the bottom of the reactor, while in Vpc mode, they were placed between two layers of glass wool in a stainless steel net at the middle of the reactor so that they acted only on the volatile products from thermal degradation of the pyrolysing materials. Experiments were performed on about 5 g of grape seed (Gs), polyethylene (PE) and their binary mixtures in the 1/1 weight ratio. The following weight ratios were used for the catalytic experiments: 5 g/1 g for Gs/Catalyst and PE/Catalyst and 2.5 g/2.5 g/1 g for Gs/PE/Catalyst.

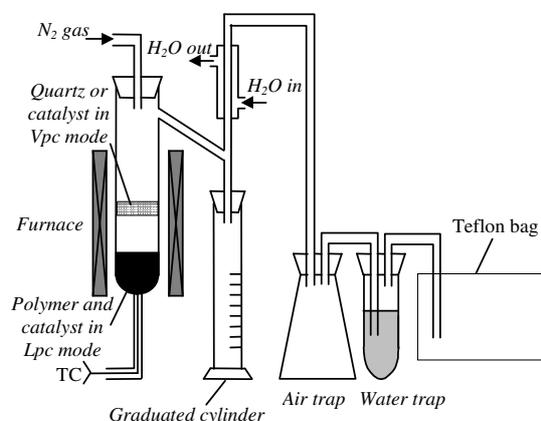


Figure 1: Schematic representation of experimental set-up for pyrolysis

Grape seeds produced by pyrolysis an aqueous phase (aq) and a highly viscous tar (oil), which is characteristic of thermal degradation of biomass, while PE gives only organic oil. The grape seed tar was dissolved in PE oil upon co-pyrolysis, while the aqueous fraction was immiscible with tar, oil, or their combination and it was easily separated by density. The aqueous fraction was extracted with ethyl ether, which allowed the qualitative analysis of the organic compounds it contained.

Catalysts were covered by coke after degradation experiments, but it was difficult to quantitatively collect the coke back from the reactor, thus the coke was considered together with the solid residue remaining after degradation at the bottom of the reactor (Res) in the calculation of the product yield.

TG analysis

The TG-MS analyses were performed on a Jupiter STA 449 F1 (Netzsch) simultaneous TGA/DSC instrument coupled with a QMS 403C Aeolos (Netzsch) MSD mass spectrometer. Samples of about 10 mg were heated by 10 °C/min up to 600 °C in an open Al₂O₃ crucible, under 50 ml/min He flow.

Product analysis

The degradation tars/oils and the ethyl ether extracts from aqueous fractions were analyzed by gas chromatography coupled with mass selective detector (GC-MSD), performed on an Agilent 6890N GC-5975 inert XL MSD instrument using a HP5-MS column (cross-linked methyl siloxane: 30 m x 0.25 mm x 0.25 µm). The following parameters were used: injector – temperature of 250 °C, split ratio of 100:1, volume of injected sample of 0.2 µl; temperature program – initial temperature of 35 °C was held for 2 min, then heated up to 300 °C by a heating rate of 10 °C/min. The identification of compounds was performed according to the library database.

The elemental analysis (C, H, N and S) of biomass was carried out by using an elemental analyzer LECO CHNS 932, according to ASTM D5291-96. The oxygen amount was calculated by the difference.

RESULTS AND DISCUSSION

TG results

Figure 2 shows the TG and DTG curves of the grape seed (alone and in the presence of PE or of

FCC and Red Mud catalysts) recorded at a heating rate of 10 °C/min under 50 ml/min He flow. It could be seen that the grape seeds started to decompose around 150 °C, then followed the loss of moisture that occurred below 100 °C with a mass loss of about 3 wt%. The DTG curve for the grape seeds shows a large peak in the temperature range of 200-500 °C, with a peak value at 390 °C and a shoulder around 350 °C. This is the sign of many overlapping processes due to the complex composition of grape seeds. The total mass loss below 500 °C was of about 69 wt%, with no appreciable mass change at higher temperatures. According to this result, it could be concluded that choosing a pyrolysis temperature of 500 °C is appropriate. Based on literature, the thermal decomposition of grape seeds can be divided into several steps: the first mass loss process is associated mainly with humidity removal (below 120 °C), the second one mainly with the decomposition of hemicellulose (150-310 °C) and the third step with cellulose and lignin degradation; however lignin degradation occurs over a broad temperature range (150-480 °C or higher),^{17,18} hence it overlaps with the degradation of the other components of biomass.

Thermal decomposition of the polyethylene occurred in a narrow temperature range, between 400 and 520 °C with a maximum rate around 475 °C; the amount of residue was negligible. Similar results were reported by other authors.¹⁹ Biomass decomposes at lower temperatures than plastics, however, the maximum degradation rate of grape seeds occurs at temperatures when the degradation of PE starts and the maximum degradation rate of PE occurs before the end of degradation for grape seeds. Therefore, interactions between the two components at co-pyrolysis are expected, despite the different nature of the two materials.

The TG and DTG curves of the Gs/PE binary mixture in 1/1 weight ratio combine the characteristics from the individual components with the particularities of the mixture. The degradation occurs in two steps, the first one corresponding to grape seeds, with a large DTG peak in the 170-370 °C temperature range and maximum around 350 °C, and the second one corresponding to polyethylene, with sharp mass loss up to 510 °C. The maximum at 390 °C in the DTG curve of grape seeds alone disappeared in the mixture and the maximum in the DTG peak of PE was shifted with about 5 °C to higher

temperatures. This is a proof of the interactions between the components of the mixture at high temperatures, the radicals formed in the initial stages of PE degradation interfering in the degradation of grape seeds, thus retarding the degradation of PE. The catalysts mixed with grape seeds favor degradation by shifting the temperature for the maximum degradation rate (the peak of DTG curves) to lower temperatures, of about 320 °C for FCC and 360 °C for RM and the end of the process to about 450 °C – Fig. 2b.

The MSD analysis of the gases evolved during TG measurements helped distinguish the formation of several compounds from the degradation of grape seeds – Figure 3. Thus, the m/z 31 signal corresponding mainly to methanol and ethanol shows a main evolution peak in 200-300 °C temperature range, with a maximum around 240 °C, and a smaller peak around 350 °C – Figure 3a. Acetic acid is formed with a maximum rate mainly around 280 °C, as shown by the m/z signal 43, 45 and 60 – Figure 3a. These signals also have variations at higher temperatures, but they are not simultaneous, thus they might correspond to other compounds. Oleic acid is formed at higher temperatures, above 300 °C, with a maximum rate around 420 °C; its evolution ends around 530 °C – Figure 3b.

The co-pyrolysis of grape seeds with polyethylene, affects the formation of degradation compounds, as shown in Figure 4. The methanol/ethanol have only a very small evolution around 290 °C, which is about 50 °C above the temperature range of their formation from grape seeds alone. The formation of acetic acid is also retarded, the m/z 60, 43 and 45 signals having shoulders around 290 °C and peak values around 360 °C.

The m/z signals characteristic of superior acids (oleic acid) in Figure 3b. are irrelevant upon co-pyrolysis of grape seeds with polyethylene, since they correspond to the hydrocarbon ion fragments of the acids, which are also specific to the hydrocarbons formed from the degradation of polyethylene. However, information on the evolution of superior acids could be obtained from the m/z 45 ($\text{H-O-C}\equiv\text{O}^+$ ion), m/z 60 (McLafferty $\text{CH}_2=\text{C}(\text{OH})_2^+$ ion) and m/z 73 signals, which are specific to the carboxylic part of the acids. These signals have clear variations in the 410-530 °C temperature range, with peak

values around 485 °C, which corresponds to the DTG peak of the Gs/PE mixture in Fig. 2a. Therefore, the formation of superior (fatty) acids

from grape seeds is retarded by the presence of polyethylene and the peak overlaps with those of the formation of hydrocarbons from the latter.

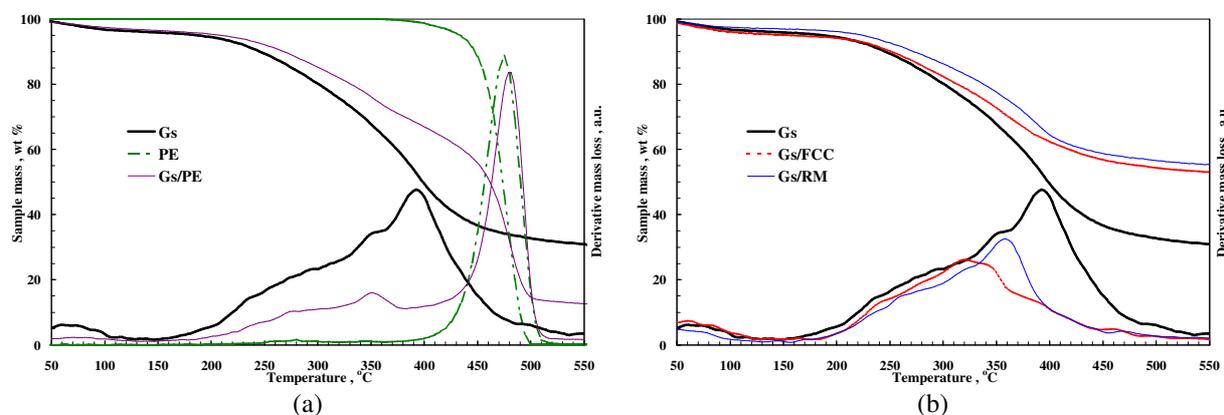


Figure 2: TG/DTG curves for grape seeds – polyethylene (a) and grape seeds – catalysts (b)

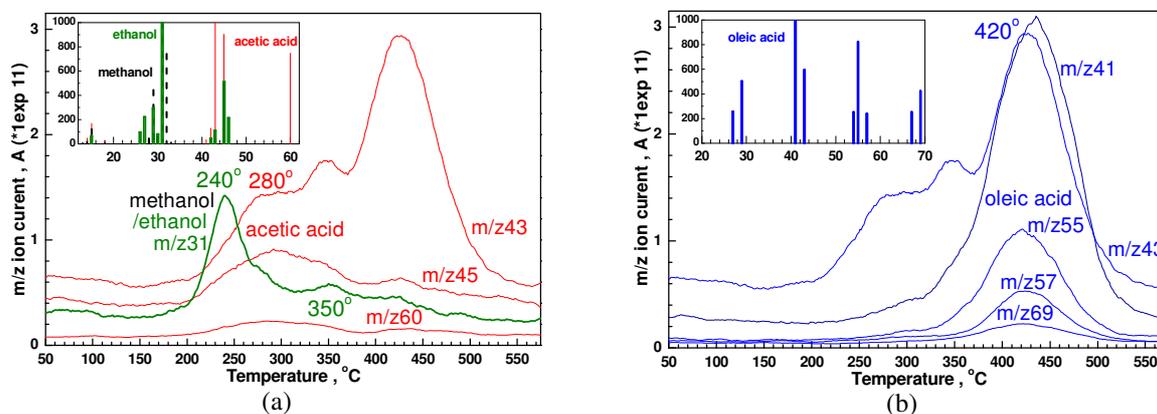


Figure 3: Evolution of methanol/ethanol and acetic acid (a) and of oleic acid (b) during TG analysis of grape seeds

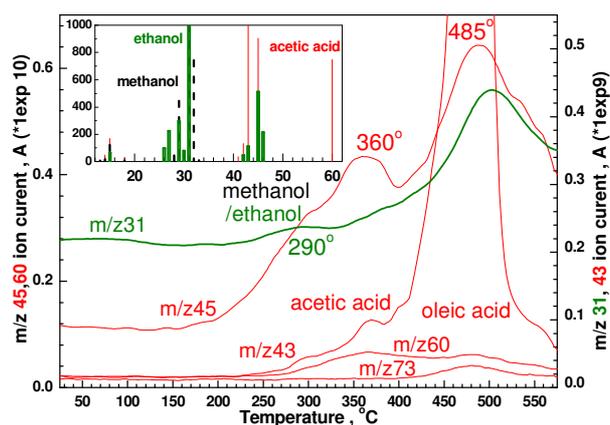


Figure 4: Evolution of methanol/ethanol and of acids during TG analysis of Gs/PE mixture

Characterization of pyrolysis oils from grape seeds and polyethylene

The pyrolysis oil from grape seeds has a complex composition, as shown by the peaks in the GC-MSD chromatogram – Figure 5. Several

classes of compounds were identified, both hydrocarbons and oxygenated compounds. Homologous series of linear aliphatic hydrocarbons from n-C₇ to n-C₁₈ were found, the lighter ones (n-C₇ – n-C₉) and the n-C₁₇

corresponding to both paraffin and olefin compounds. Only n-C₁₂ and n-C₁₃ compounds were not found, but this might be due to the difficult separation of numerous peaks. Carboxylic acids were also identified, in two groups: the first and the most important ones in terms of peak were the palmitic (C₁₆), oleic (C₁₈=), stearic (C₁₈) and linoleic (C₁₈=) fatty acids, together with some of their methyl esters (methyl palmitate, methyl stearate), while the second group contained lighter C₁ – C₆ acids. The light carboxylic acids and the homologous series of paraffins and olefins might come from thermal scission of the heavier fatty acids. However, acetic acid, obtained in the highest amount among

light acids, is produced mainly from the degradation of lignin in grape seeds.

Furfural and methylfurfural are compounds resulted from the degradation of the cellulose part or of hemicelluloses in the grape seed composition. Oxygenated aromatic compounds are typical degradation products of lignin, having the phenol-, guaiacol- and catechol-type structures, as listed in Table 2. It was interesting to observe the presence of C₁ – C₅ derivatives of benzene (column 2 in Table 2), their presence suggesting partial deoxygenation of the lignin structure, due to interactions with other components in the grape seeds.

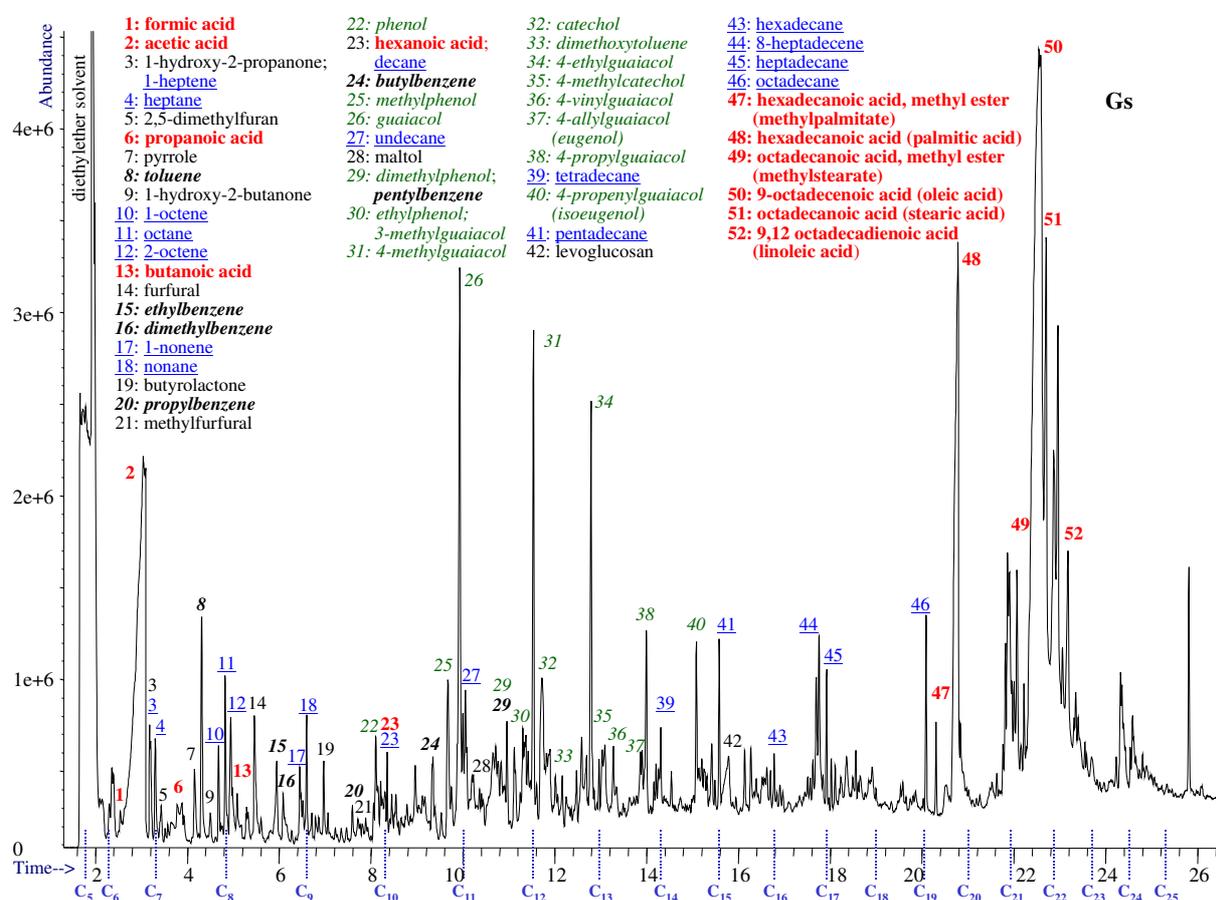


Figure 5: GC-MSD chromatogram of grape seed pyrolysis oil

The oil obtained from the pyrolysis of PE showed the typical shape of homologous series of linear saturated and monounsaturated hydrocarbons in a broad range from n-C₅ to n-C₂₅, as shown in Figure 6a. These come from the random scission of long macromolecular chains,

having very few weak points able to preferably initiate the breaking of bonds.

The GC-MSD chromatogram of the pyrolysis oils from the grape seeds/polyethylene mixture is dominated by the degradation compounds of PE. Since grape seeds also produced homologous

series of paraffins and olefins (underlined compounds in Fig. 5), they could not be distinguished from the ones obtained from the degradation of polyethylene. The aromatic derivatives from grape seeds (***bold italic*** compounds in Fig. 5 and Table 2) are also products of PE degradation. Acetone and guaiacol with its methyl- and ethyl- derivatives (compounds 2, 26, 31, 34 in Fig. 5 and Table 2) from the lignin part of grape seeds were observed

in the corresponding selective ion chromatograms (m/z 60, 109 and 124, 123 and 138, 137 and 152, respectively), but they were covered in the total ion chromatogram by the peaks of hexane, undecane, dodecane and tridecadiene, respectively. Only the peaks of palmitic, oleic and stearic fatty acids from the degradation of grape seeds were distinguished among the numerous peaks of PE degradation compounds, as shown by the details in Fig. 6b.

Table 2
Main lignin-derived compounds found in pyrolysis oil from grape seeds

N Benzene type	No Phenol type (P)	N Guaiacol type	No Catechol type	Side chain
	22 <i>phenol</i>	26 <i>guaiacol</i>	32 <i>catechol</i>	H
8 <i>toluene</i>	25 <i>methylphenol</i>	31 <i>methylguaiacol</i>	35 <i>methylcatechol</i>	CH ₃
16 <i>dimethylbenzene</i>	29 <i>dimethylphenol</i>			2 x CH ₃
15 <i>ethylbenzene</i>	30 <i>ethylphenol</i>	34 <i>ethylguaiacol</i>		CH ₂ -CH ₃
		36 <i>vinylguaiacol</i>		CH=CH ₂
20 <i>propylbenzene</i>		38 <i>propylguaiacol</i>		CH ₂ -CH ₂ -
				CH ₃
		37 <i>eugenol</i>		CH ₂ -
				CH=CH ₂
24 <i>butylbenzene</i>		40 <i>isoeugenol</i>		CH=CH-CH ₃
29 <i>pentylbenzene</i>				C ₄ H ₉
				C ₅ H ₁₁

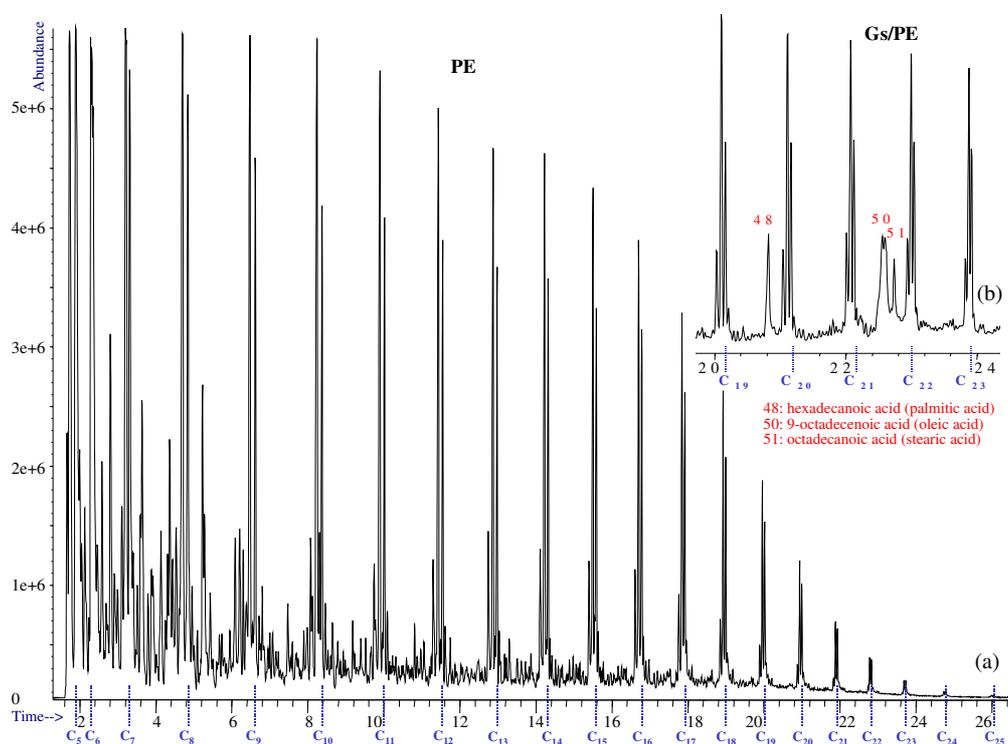


Figure 6: The GC-MSD chromatogram of pyrolysis oils from PE (a) and Gs/PE mixture (b)

Catalytic pyrolysis

The product yield for thermal and catalytic degradation of grape seeds at 500 °C is shown in

Figure 7a. Grape seeds gave about 21 wt% oil, 23 wt% aqueous fraction and 15 wt% gases, leaving 41 wt% residue. In an experiment, the grape seeds

were subjected to repeated Soxhlet extractions in ethyl ether, water and ethanol to remove useful fractions as extracts which exhibit antioxidant properties and can be used to prevent health problems. The extraction shifted about 3 wt% of material balance from gases to the aqueous fraction and decreased the oil yield with about 15 wt%, which was found in the increase of residue amount. This was due to the removal of organic compounds from the grape seeds by solvent extraction. The catalysts decreased oil yield to about 16-17 wt%, with no significant difference

among them; however, it was clear that the Vpc mode increased the amount of the aqueous fraction to the detriment of gaseous products. The amount of residue increased, mainly due to the coke formation on catalyst. The coke was in the highest amount for FCC in the Vpc mode, which gave the lowest gas yield and the highest amount of aqueous fraction. Therefore, coke formation could be related to the dehydration activity of the catalysts, as also reported by French and Czernik.²⁰

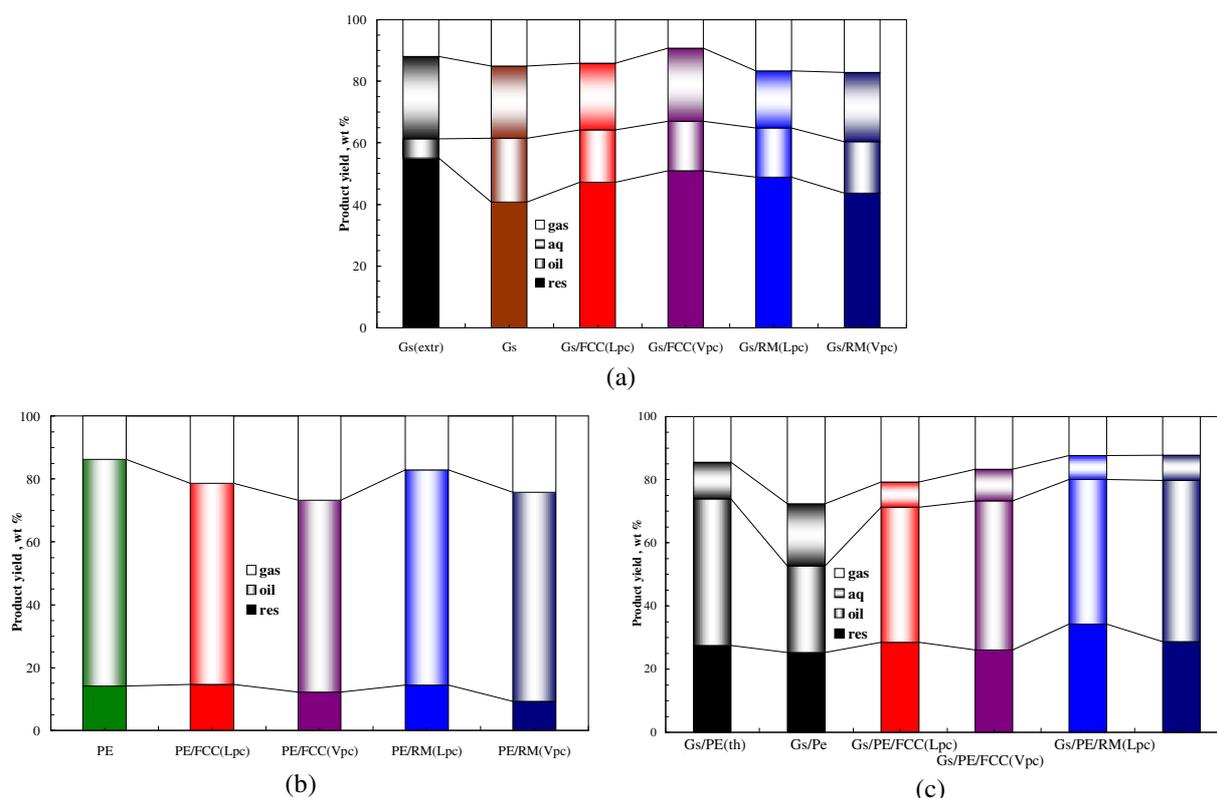


Figure 7: Product yield from thermal and catalytic of grape seeds (a), polyethylene (b), and their 1/1 wt mixture (c)

The linear hydrocarbon structure of PE led to a high yield of pyrolysis oil (72 wt%), which was different from grape seeds – Figure 7b. Gases and residue were in similar amounts (about 14 wt%). The amount of residue was increased in our experimental set-up by the fact that the outlet of the reactor was about 7 cm above the exit of the furnace and the colder region in between acted similarly to a distillation column, refluxing part of the volatile products. Therefore, the heavy degradation products that were volatile at the reaction temperature, but could not pass the colder region before the outlet remained inside the

reactor as residue. Both FCC catalyst and Red Mud decreased the oil yield, while favouring gas formation. This is in good agreement with other reports, which showed higher gas yields when using FCC or Red Mud for catalytic degradation of plastics.^{21,22} The residue amount was smaller for the Vpc mode, compared to thermal degradation, while for Lpc, it was only slightly higher. However, considering the coke formation on catalysts, we can say that the PE residue was also decreased in the Lpc/PE mode. This is a proof of the cracking effect of FCC and RM, that shifts part of the heavy molecular weight compounds

from residue to lighter ones in oil but mainly converts the light compounds from oil to much lighter ones in gases. Vpc mode is more effective than Lpc, as proved by lower oil yields and higher gas amounts. Similarly, FCC catalyst showed more cracking activity than Red Mud.

The product yields for thermal and catalytic co-pyrolysis of grape seeds with PE at 500 °C are given in Figure 7c. For the sake of comparison, the theoretical product yield for thermal co-pyrolysis, calculated by the additive rule based on individual components, is also shown – Gs/PE(th). The experimental and theoretical yields are different, showing that interactions occur between grape seeds and polyethylene at high temperatures of degradation. The oil yield decreased from 46 to 27 wt%, while the aqueous fraction and gases almost doubled (they increased from 12 and 14 wt% to 20 and 28 wt%, respectively). The amount of residue had only small changes showing that interactions occur mainly between the primary products of degradation, but not between grape seeds and polyethylene materials. The main source of interaction is the high hydrogen content of polyolefinic plastics that are an excellent hydrogen source for the biomass rich in oxygen.²³ Catalysts strongly increased the oil yields to 43-51 wt% to the detriment of the aqueous phase (8-10 wt%) and of gaseous products (12-20 wt%), but with the consequent formation of supplementary coke. Contrary to the pyrolysis of PE, the Vpc mode gave more oil and less gas, compared to the Lpc mode, while residue decreased for both contact modes. The aqueous phase was higher for Vpc, similar to the pyrolysis of grape seeds alone. Red Mud gave more oil yields, while decreasing the amounts of the aqueous phase, gas and residue. This was also contrary to the pyrolysis of PE alone, where FCC showed higher activity. Therefore, the selectivity of pyrolysis products can be controlled by the catalyst type, but also by the contact mode, as also reported by Chaianansutcharit *et al.*²⁴

CONCLUSION

The pyrolysis of grape seeds, alone or mixed with polyethylene, was considered in this study, thermally and using Red Mud and FCC catalysts in two contact modes (liquid and vapour). Thermogravimetric analysis was performed to determine the temperature domains for the degradation of the two materials and MSD

analysis of the evolved volatile products helped to distinguish the formation of several compounds with increasing temperature. The degradation of grape seeds started around 150 °C, while polyethylene was thermally stable below 400 °C. The degradation of polyethylene was slightly retarded upon co-pyrolysis, showing interactions between the components. The formation of fatty acids from grape seeds was also retarded, overlapping with the formation of hydrocarbons from polyethylene.

Pyrolysis was performed at 500 °C, which assured the total decomposition of both materials and caused some interactions between them, with effects on product yield. The composition of pyrolysis oils was determined by GC-MSD analysis. Grape seeds produced compounds typical of biomass (furfural and methylfurfural from the cellulose and hemicelluloses part and phenol-, guaiacol- and catechol-type structures from the lignin part) and acids (especially fatty ones) from the vegetable oil contained in the seeds. Light acids and homologous series of light hydrocarbons were also produced as degradation compounds of heavy oils, while some aromatic hydrocarbons might be the result of partial deoxygenation of lignin structures.

Red Mud and FCC catalysts enhanced the degradation and changed the product yield depending on the phase contact mode (liquid or vapour) in which they were used. The oil amount significantly increased upon catalytic pyrolysis. It has been established that the selectivity of pyrolysis products can be controlled by the catalyst type, but also by the contact mode.

ACKNOWLEDGEMENTS: This research was supported by the European Union through the “PIRSES-GA-2009-247550 – Biofuel” grant of the FP7 program.

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