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Investigation of thermal and catalytic degradation of polystyrene waste into styrene monomer over natural volcanic tuff and Florisil catalysts

Research Article

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Abstract: Thermal and catalytic degradation of polystyrene waste over two different samples of natural volcanic tuff catalyst comparative with Florisil catalyst has been carried out in order to establish the conversion degree into styrene monomer. The polystyrene waste (PS) was subjected to a thermal degradation process in the range of 380-500°C in presence of studied catalysts in a ratio of 1/10 in mass, catalyst/PS. The catalysts were characterized by N_2 adsorption-desorption isotherms (BET), Scanning Electron Microscopy (SEM) and Fourier-transform infrared spectrometry (FTIR). Influences of temperature and type of catalysts on the yields and on the distribution of end-products obtained by thermal and catalytic degradation of polystyrene waste have been studied. The maximum yields of liquid products were obtained at 460°C degradation temperature and were calculated between 83.45% and 90.11%. The liquid products were characterized by gas chromatography mass spectrometry (GC-MS) and FTIR analytical techniques. The GC-MS results showed that the liquid products contained styrene monomer up to 55.62%. The FTIR spectra of liquid products indicated the specific vibration bands of the functional groups of compounds of liquid products. The amounts of styrene monomer obtained were influenced by structural and textural properties of studied catalyst and the contribution on product distribution is discussed.

Keywords: *Polystyrene waste • Catalytic degradation • GC-MS • Styrene monomer • Volcanic tuff*

1. Introduction

Plastics are the most versatile material in our modern society and contributes to our life in many aspects like economic activity, quality of life and jobs [1]. Polystyrene is an inexpensive and hard plastic material, very common in our everyday life and with a wide range of applications such as packaging, toys, and the housings of items such as hairdryers, computers, kitchen appliances, customer goods, *etc*. Disposal of these products creates serious environmental pollution because of their non-degradable nature. The polystyrene waste (PS) represents around 10 wt.% of total plastic waste steam [2,3]. Therefore their recycling is important for both economical and ecological reasons. The conventional method for the treatment of plastic waste such as polystyrene is pyrolysis, which involves thermal decomposition in the absence of air to produce pyrolysis oils or gases and to recover the monomer or other valuable chemicals [4].

The liquid and gaseous products resulted from the degradation process of polystyrene is highly dependent on the reaction conditions. Catalytic degradation using

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suitable catalysts has the ability to control both the product yield and product distribution in addition to reduced reaction temperature. This advantage leads to the high contents of products having higher commercial value [2,3].

Thermal and catalytic pyrolysis of polystyrene was reported in the literature [5-23]. Polystyrene could be converted into styrene over catalysts by simple thermal cracking at relatively low temperature. The thermal degradation process of polystyrene is highly dependent on the reaction conditions: temperature, reaction time, reactor type, the presence of catalysts, etc. At low temperatures products mainly consist of liquid compounds (mono aromatic). At higher temperatures, gas and coke yields are higher and the liquid fraction has significant aromatics (dimer, trimer) [2,3,5,10,13].

The polystyrene pyrolysis was investigated at a relatively low temperature range of 370 to 400°C using a batch-type stirred vessel. The main products were single aromatic species (styrene ca. 70 wt.%, α-methylstyrene, toluene) and double aromatic species (1,3-diphenylpropane and 1,3-diphenylbutene) [5]. The study of polystyrene degradation was made by continuous distribution kinetics in a bubbling reactor [6]. The pyrolysis at 550°C of polystyrene waste in a fluidized-bed reactor generated the residue that contains 19-20% for oil yields and 10-11% for styrene monomers [7,8].

Thermal decomposition of expanded polystyrene in a pebble bed reactor produced a liquid product yield of 91.7% at 500°C and a styrene yield of 85.5% using ceramic pebbles [9].

Several studies have been conducted on catalytic degradation of polystyrene over different solids like metallic oxides (silica-alumina, K_2O, CaO, BaO, SiO_2, Al_2O_3, CuO/Al_2O_3, alumina or silica supported transition metals) [10-13,21], zeolites (HNZ, ZSM-5, FCC, clinoptillolite, Al-MCM-41, dealuminated HY) [7,14,15,17,20], mesoporous materials (K_2O/Si-MCM-41, K_2O-BaO/MCM-4, MCM-41 from natural sepiolite) [18,19,24], clays (halloysite, albite, montmorillonite, and pyrophyllite [16,22,23]. The yields and distributions of end-products are mainly influenced by structural and textural properties of catalysts [7,10-24].

Styrene monomer recovery from polystyrene waste was studied in supercritical solvents (benzene, toluene, ethyl benzene, *p*-xylene). The process was performed in the presence of hydrogen at elevated temperature and pressure and with metal oxide as catalysts [21,25]. The co-pyrolysis of waste polystyrene with coal was investigated on high temperature obtained by microwave-copper interaction [26,27].

Gas chromatography with mass spectroscopy detector (GC-MS), gas chromatography with flame ionization detector (GC-FID), and Fourier transform infrared spectroscopy (FTIR) are the most used techniques to establish the characteristics of products (liquid, gas and residue) from thermal degradation of polymeric compounds [5-30]. The advantages of the use of high resolution GC-MS technique in analysis of polymeric degradation products include a better separation of multicomponent product mixtures. The more reliable identification and the more precise quantitative results are made by more characteristic measured mass spectra and by decrease of base-line *versus* increase of unresolved GC peaks [31]. Decomposition of the carbon chain from plastic waste could be monitored by GC and both by FTIR and SEC techniques in the case of volatile fractions and residues. FTIR spectra of the products obtained indicate the presence of functional groups specific to hydrocarbon components [12,29]. Other modern techniques used for investigation of hydrocarbon fraction from waste plastic recycling has been Raman spectroscopy, size exclusion chromatography (SEC), energy-dispersive X-ray fluorescence spectroscopy, thermal analysis, and pyrolysis-GC with mass spectrometry detection (Py-GC-MS) [28,29].

The use of catalysts in the pyrolysis process of plastic waste determines the good selectivity for the formation of hydrocarbons with higher market values and use of lower temperatures. The search of “cheap catalysts” for pyrolysis of plastic wastes is of the most interest from an industrial implementation point of view and may condition the economy of the process [32].The catalyst cost, type and amount represent key factors in the economy of catalytic processes because, in a continuously operating plant, it is necessary to have a high amount of catalyst. Therefore, natural catalysts are used in this purpose since their textural properties, such as surface area, particle size and pore size distribution plays an important role in end-product distribution.

The objective of this work was to study the thermal and catalytic degradation of polystyrene waste over two samples of natural volcanic tuffs catalyst compared with Florisil catalyst. The catalytic performance of these catalysts at degradation of polystyrene waste was evaluated in order to establish the best conversion degree into styrene monomer. The liquid products obtained were analyzed by GC-MS and FTIR analytical techniques for determination of their hydrocarbon compositions. Influences of temperature and type of catalysts on the yields and on the distribution of end-products obtained by thermal and catalytic degradation of polystyrene waste were investigated. The use of

the Romanian natural volcanic tuff catalyst for study of thermal and catalytic degradation of polystyrene waste could be a suitable way for cost reduction of catalytic process and to obtain an important quantity of styrene monomer.

2. Experimental procedure

2.1. Materials

The sources of polystyrene waste (PS) were vessel detergent boxes and disposable glasses and plates which were cut into small pieces approximately 5×5 mm.

The catalysts used in this study were two zeolitic volcanic tuff samples (Tuff 1, Tuff 2) and Florisil. The natural volcanic tuff samples are provided from the same area (Marşid, county Sălaj, Romania) but they have different structural and textural properties and chemical compositions. The volcanic tuff from Mârsid is one of the representative species of the volcanic tuff in Romania, having a clinoptilolite content ranging from 60% to 70% [33].

The Florisil (activated magnesium silicate) is a chromatographic material manufactured by *Raluca Ripan* Institute for Research in Chemistry, Cluj-Napoca, Romania, and contains SiO_2(~83%) and MgO (~15%) and small quantities of Na_2SO_4. Using the Florisil as catalyst has been chosen due to its structural and textural catalytic properties and the high content of SiO_2 that are very similar with those of volcanic tuff samples.

The catalysts were subjected to a heating treatment in an oven in two stages. The first was made at 200ºC for 2 hours that removed the adsorbed water from the mesopores, then followed the second heat treatment at 500ºC for 5 hours to activate the active centers. Then the catalysts were kept in a desiccator for the experiments.

The surface area and porosity characteristics of the calcined catalysts were determined by nitrogen adsorption-desorption isotherms at 77 K using a Micromeritics TriStar II 3020 instrument. Firstly the catalysts were decontamined under nitrogen flow at 160ºC for 5 hours. For investigating the surface area and porosity of catalyst powders, the procedure consists of a gradual increase in adsorption gas pressure to the saturation value, when gas condensation occurs. With increasing pressure, an increase in the amount of gas adsorbed on the surface and pores of the powder occurred. The surface area was determined by the BET (Brunauer-Emmett-Teller) method. The micropore area and volume were obtained applying the t-plot (de Boer) method. For determination of meso- and macropore area and volume was applied the BJH (Barrett, Joyner, Halenda) method on isotherm desorption branch.

External surface, morphology and structure of catalysts were visualized by Scanning Electron Microscopy (SEM) and the chemical compositions were determined by the EDAX (Energy Dispersive Analysis of X-Rays) method using a QUANTA 133 Electron Microscope (FEI Company).

Structural information of catalysts were obtained by FTIR spectra registered with a JASCO-FTIR 610 Fourier-transform infrared spectrometer (FTIR) in the 4000-400 cm^{-1} wave number range, using the KBr pellet technique.

2.2. Thermal degradation procedure

Thermal degradation of the polystyrene waste was performed in a tubular glass reactor (175×33 mm ID) heated externally by an electric furnace. A thermometer with thermocouple (K type) was fixed inside the reactor and the temperature was controlled by external PID controller. The PS and the catalyst in a mass ratio of 10/1, w/w, was added in the reactor. Before starting the experiments, the nitrogen gas was continuously passed through the installation with a flow rate of 30 mL min^{-1} for 10 minutes to remove the air. Then it was followed by the thermal decomposition step that was heated at a rate of 20ºC min^{-1} up to the desired temperature. The formed gaseous products passed through a water cooled condenser (0-4ºC) and the condensable gases were collected as a liquid product. The incondensable gases were collected in a special bag as a gaseous product. The small quantity of residue and the used catalyst remained in the glass reactor. The thermal degradation procedure was carried out at different temperatures in the range of 380-500°C.

The yields of obtained products were calculated. The identification and quantification of the compounds from liquid products was performed by GC-MS and FTIR analysis.

2.3. Analysis of products

The liquid and solid (residue and catalyst) products were weighed directly. The yields of obtained products by catalytic degradation of PS (L – liquid products, R – residue and G – gaseous products) were calculated using Eqs. 1-3. The yields of gaseous products were determined by the difference:

$$L(wt.\%) = \frac{m_L}{M_{PS}} \cdot 100 \quad (1)$$

$$R(wt.\%) = \frac{m_R}{M_{PS}} \cdot 100 \quad (2)$$

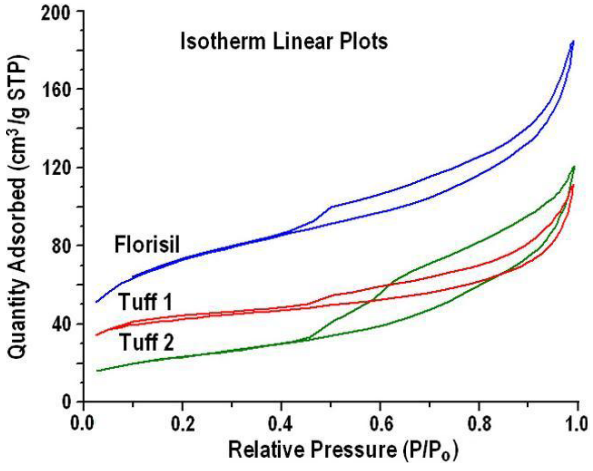


Figure 1. The N_2 adsorption–desorption isotherms at 77 K of the studied catalysts.

$$G(wt.\%) = 100 - (L + R) \quad (3)$$

where m_L is the weight of liquid product (g), m_R the weight of residue (g) and M_{PS} the weight of polystyrene waste (g).

The GC-MS analysis of liquid products was performed by a Hewlett Packard HP 5890 Series II GC gas chromatograph interfaced to a Hewlett Packard 5972 Series mass selective detector using a DB-5MS capillary column (30 m × 0.53 mm ID x 1.50 μm film thickness) with the following temperature program: the initial temperature of 40°C was held for 10 min, increased by 4°C min^{-1} at 280°C and maintained at this final temperature for 10 min. The helium was the carrier gas. Temperature of the injector was 250°C. The volume of injected sample was 1 μL (split 10:1). MS mode was carried out in full scan, with a scan range of 10-700 amu and a scan speed up to 1800 amu s^{-1}. The ionization intensity of 70 eV and the multiplier voltage of 1823.5 V were used. The acquisition of chromatographic data was performed by means of the HPchem software. All mass spectra obtained by GC-MS were interpreted based on an automatic library search (DATABASE/wiley6.1).

The liquid products were also measured by spectrometric infrared technique with a JASCO-FTIR 610 Fourier-transform infrared spectrometer (FTIR) in the 4000-400 cm^{-1} wave number range, using the liquid film technique. The FTIR spectra of all the studied liquid products were registered at room temperature.

3. Results and discussion

3.1. Catalyst characterization

The nitrogen adsorption-desorption isotherms of the catalysts were presented in Fig. 1.

The nitrogen adsorption-desorption isotherms shown in Fig. 1 are IV isotherm type combined with II isotherm type of adsorption branch (adsorption in case of absence capillary condensation), according to the International Union of Pure and Applied Chemistry (IUPAC) classification [34].

The meso- and microporous nature of these catalysts is indicated by the relative high adsorption volume at low relative pressure ($P \cdot P_0^{-1} < 0.1$) and by the narrow hysteresis loop (especially Tuff 1 and Florisil). When the relative gas pressure increased, the adsorption of gas molecules is taking place in pores. In the first stage, the micropores are filled, and in the second stage, the meso- and macropores are filled showing adsorption-desorption isotherm behaviour with its characteristic H4 hysteresis loop (IUPAC) [34]. This type of hysteresis loop is often associated with narrow slit-like pores that are usually found in solid aggregates consisting of parallel plates that are not rigidly connected together or with agglomerates of particles.

In Table 1 and Fig. 2 are presented the surface area and porosity characteristics and the pore size cumulative / derived distribution curves (pore volume, pore area) of the catalysts used for thermal degradation of polystyrene waste respectively.

The Florisil catalyst has the highest value for BET surface area of 246.60 $m^2 g^{-1}$ and it also has the highest value of meso- and macropore volume of 0.250 $m^2 g^{-1}$. That fact represents an important feature for catalytic activity. The distribution curve of pore size volume shows that the mesopores with diameter between 35-50 Å are predominant and occupy the largest volume. The average pore diameter is 66 Å and suggests a small number of macropores.

Tuff 1 catalyst presents half of the surface area than Florisil, respectively 138.31 $m^2 g^{-1}$. It shows a heterogeneous pore volume distribution curve. Predominant are mesopores with diameter between 35-50 Å. They have a smaller volume than in the Florisil sample. The distribution curve of pore volume suggests heterogeneous macro porosity between 50-1100 Å. That can be explained by an average pore diameter of 95 Å.

Tuff 2 catalyst, has a smaller surface area of 82.26 $m^2 g^{-1}$ and presents a bi-modal pore volume distribution curve. That suggests two types of pore dimensions: mesopores between 35-50 Å and macropores between 50-75 Å. The macropores of Tuff 2 catalyst occupy a larger volume then Tuff 1 catalyst (see Fig. 2). The average pore diameter of Tuff 2 catalyst is 74 Å.

The chemical compositions of the calcined catalysts were determined from EDAX (Energy Dispersive Analysis of X-Rays) spectra reported in Fig. 3.

Table 1. Surface area and porosity characteristics of the studied catalysts.

Catalyst	Specific surface area, BET[a], $m^2\ g^{-1}$	Micropores area[b], $m^2\ g^{-1}$	Micropores volume[b], $cm^3\ g^{-1}$	Meso- & macropores area[c], $m^2\ g^{-1}$	Meso- & macropores volume[c], $cm^3\ g^{-1}$	Average meso- & macropores diameter[c], Å
Florisil	246.60	77.35	0.01680	150.67	0.250	66
Tuff 1	138.31	72.05	0.02950	56.24	0.133	95
Tuff 2	82.26	29.14	0.00510	115.79	0.214	74

[a]BET method; [b]t-plot method; [c]BJH desorption method

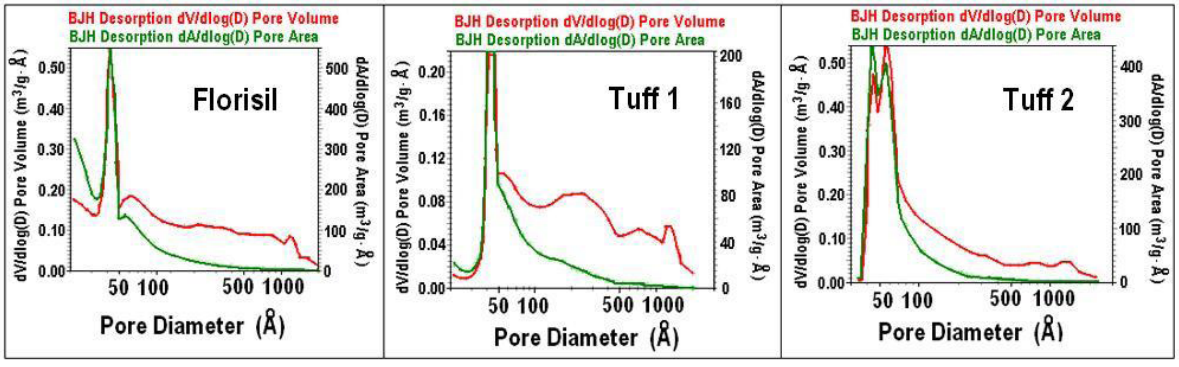
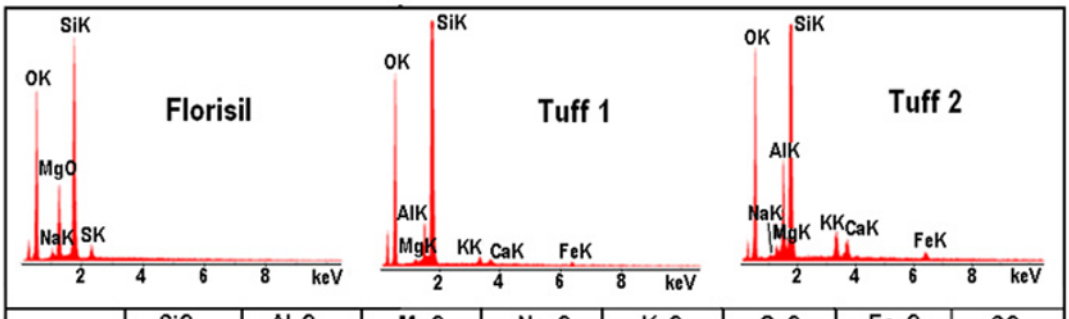


Figure 2. Pore size cumulative /derived distribution curve of the studied catalysts.



	SiO_2	Al_2O_3	MgO	Na_2O	K_2O	CaO	Fe_2O_3	SO_3
Florisil	83.18	-	15.65	0.53	-	-	-	0.64
Tuff 1	79.87	12.68	1.16	0.34	2.31	2.04	1.60	-
Tuff 2	75.70	14.27	1.80	0.51	3.39	2.38	1.95	-

Figure 3. EDAX spectra and chemical composition of the studied catalysts.

Chemical composition of studied catalysts shows that SiO_2 and Al_2O_3 are main components in volcanic tuff samples and also contain minor amounts of Na_2O, MgO, Fe_2O_3 and other oxides. In the case of Florisil catalyst, the main components are SiO_2 and MgO.

SEM images of catalysts used in thermal degradation of polystyrene waste were carried out in order to observe the morphology of these materials and are presented in Fig. 4.

Fig. 4 shows the structure of Florisil and volcanic tuffs catalysts which is constituted by different size particles and larger crystals. The morphology and different shapes are formed by agglomeration of the macropores. This confers to catalysts a highly heterogeneous internal structure. All of the measurements were carried out at the same full scale of 30 μm for better correlation. Micro porous structure is not observed by SEM.

The FTIR spectra of studied catalysts are presented in Fig. 5. FTIR spectra can be useful in obtaining the structure information about catalysts, the channel size and the cation substitution (Si^{+4} by Al^{+3}) in the tetrahedral sites of zeolite minerals [35,36].

In Fig. 5 it can be observed, like in the case of silicates [37], that the Si–O vibration are evidenced by the very strong absorption bands from 1106 and 1049 cm^{-1}, while the bands at 523 and 470 cm^{-1} appear due to Al–O–Si

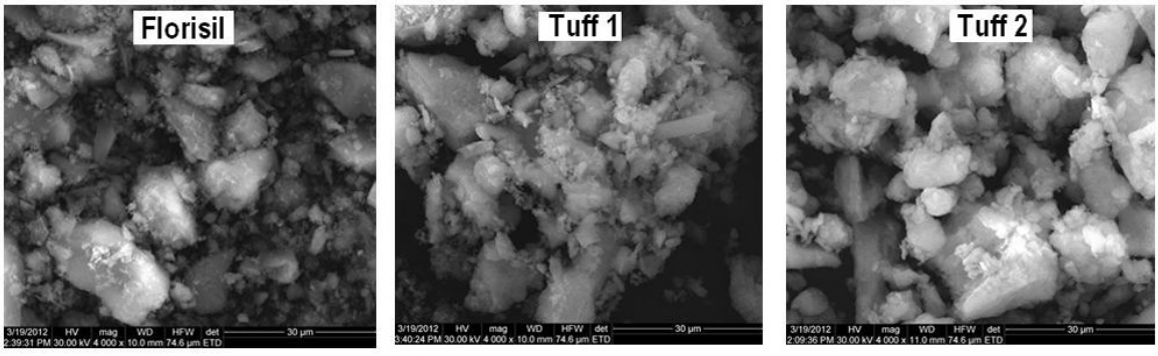


Figure 4. SEM microphotographs of the studied catalysts.

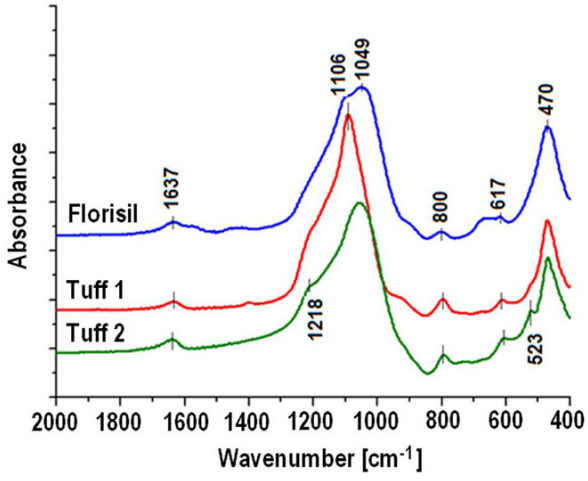


Figure 5. FTIR spectra of the studied catalysts.

and Si–O–Si bending vibrations, respectively. The band at 617 cm^{-1} is assigned to coupled Al–O and Si–O out-of-plane vibrations. The weak band from 800 cm^{-1} occurs due to the vibrations of internal oxygen bridges Si-O-Si. The FTIR band from 1637 cm^{-1} represents H–O–H bending vibration of absorbed water [37,38].

3.2. Yields of products

The *influence of temperature on yields of products* has been studied by degradation of PS in the presence of Tuff 1 catalyst in a ratio of 1/10 in mass, catalyst/PS, at the temperature range between 380°C and 500°C. This study was carried out in order to select the most appropriate temperature to compare the behaviour of all the used catalysts.

The thermal degradation products obtained were classified in three classes of products: liquid, gas and residue. As known, the yields of these products depend on many parameters such as: temperature, polymer and catalyst type, experimental reactor, residence time of volatiles in reactor, *etc.* [2,3,5,10,12].

The yields of the obtained products at thermal degradation of PS in presence of Tuff-1 catalyst (PS-Tuff 1), calculated according to the Eqs. 1-3, are presented comparatively in Fig. 6a. The code of liquids is according to the used catalyst for PS degradation are as follows: PS-Florisil (blue), PS-Tuff 1 (red) and PS-Tuff 2 (green).

The results presented in Fig. 6a show that the yields of liquid products obtained by the thermal degradation of the polystyrene waste in presence of Tuff 1 catalyst have high values between 73.71% (at 380°C) and 84.48% (at 460°C).

At 380°C, a low liquid yield was obtained because the temperature is not high enough to decompose the entire PS sample. The solid residue obtained of 21.56% contains unconverted polymer. Until 460°C, the yield of liquids increases with increasing degradation temperature while the residue yield decreases with increasing temperature. At low temperature, 380-410°C, was obtained clear liquids with low viscosity. With an increase of the temperature to 430-500°C, the liquids became viscous because waxy products were formed.

At high temperatures of 500°C, it can be observed that the liquid yield decreases and consequently the gas production increases. That can be explained by the stronger cracking of C−C bonds that takes place at this higher temperature, and formation of more non-condensable gaseous products with shorter carbon chains [2].

Based on these results the temperature of 460°C is the temperature that leads to the greatest amount of liquids (best conversion degree of PS) and was selected for studying the influences of the catalyst types on thermal degradation of polystyrene waste.

Influence of catalysts on the yields of products obtained from thermal degradation at 460°C of PS are presented in Fig. 6b. Thermal degradation of PS at 460°C in the presence of different types of catalysts produces high yields of liquid product in the range of 83.45% and 90.11%. In order to compare the effect of catalysts on the yield products, the structural and textural properties of the catalysts were taken into consideration.

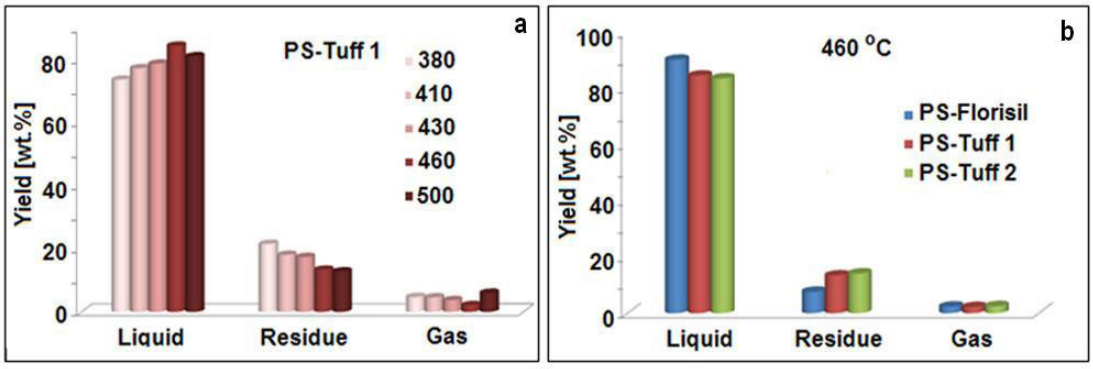


Figure 6. The influences of temperature and catalysts type on yields of products obtained thermal degradation of PS.

The highest yield of liquid product of 90.11% has been obtained in presence of Florisil as catalyst. These results are due to textural properties of catalyst such as the highest BET specific surface area of 246.60 $m^2 g^{-1}$. Also, the Florisil contains the largest amount of silica of all catalysts. Thermal degradation of PS on silica gel, a solid acid catalyst, determined a high yield of liquid product and styrene monomer, respectively [12].

In the case of thermal degradation of PS in presence of natural volcanic tuff samples, the yields of liquid product obtained were 84.48% for Tuff 1 and 83.45% for Tuff 2, respectively.

3.3. Analysis of liquid products

3.3.1. GC-MS analysis

The liquid products have been analized by GC-MS in order to identify and quantify the hydrocarbons present and to find the conversion degree in styrene monomer. The quantification was made by area percentage of TIC (total ion chromatogram). All liquid products were registered with GC-MS chromatograph.

Fig. 7 shows the GC-MS chromatograms of liquid products obtained by thermal and catalytic degradation of PS.

For all liquid products, the main compounds were toluene (**1**, 6.15 min), ethylbenzene (**2**, 11.97 min), styrene monomer (**3**, 17.03 min) (up to 54.16%), 1-methylethylbenzene (**4**, 18.71 min), α-methylstyrene (**5**, 23.45 min) and 1,1'-(1,3- propanediyl)bis benzene (**6**, 50.79 min). In all cases, the styrene monomer is the major degradation product.

The compounds were identified by comparison of their mass spectra with those from the DATABASE/ wiley6.1 spectra library.

Besides these main compounds of the studied liquid products, the GC-MS chromatograms contained some small peaks of other compounds found in smaller quantities. The peaks that appear in chromatograms after 50 min correspond to other dimer compounds.

The *influence of temperature on distribution of compounds from liquid products* obtained from thermal degradation of PS in presence of Tuff 1 catalyst is presented in Fig. 8a. The code of liquids is according to the used catalyst for PS degradation: PS-Florisil (blue), PS-Tuff 1 (red) and PS-Tuff 2 (green).

The results show that the temperature affects the quantity of the obtained styrene monomer. With increase of the degradation temperature, up to 460°C, the quantities of styrene monomer increase between 37.12% to 54.16% and quantities of ethylbenzene decrease between 26.8 % to 14.83%.

The largest quantity of the styrene monomer of 54.16% was obtained from thermal degradation of PS in the presence of Tuff 1 catalyst at a temperature of 460 °C. At 500°C, it can be observed that a decrease of styrene amount corresponded with increase the 1,1'–(1,3-propanediyl)bis benzene (dimer) amount.

The *influence of catalysts on distribution of compounds from liquid products* obtained from catalytic degradation at 460°C of PS is presented in Fig. 8b.

The GC-MS results show that the quantity of styrene monomer obtained by the thermal degradation at 460°C of PS were influences by the type of used catalyst.

The largest quantities of the styrene monomer of 55.62% are obtained from thermal degradation at 460°C of PS in the presence of Florisil catalyst, the most efficient catalyst. These results are due to the structural properties of the Florisil catalyst that presents a high BET specific surface area value of 246.60 $m^2 g^{-1}$ and also a highest value of meso- and macropore volume of 0.250 $m^2 g^{-1}$ (see Table 1). Also the Florisil contains a high amount of MgO that determines a high catalytic activity and good selectivity to styrene monomer [24].

With respect to the volcanic tuff catalysts, the Tuff 1 sample determines the highest quantity of monomer styrene of 54.16%. Also, important amounts of ethyl benzene of 12.7% and methyl styrene of 12.33%, respectively, were obtained in the presence of this

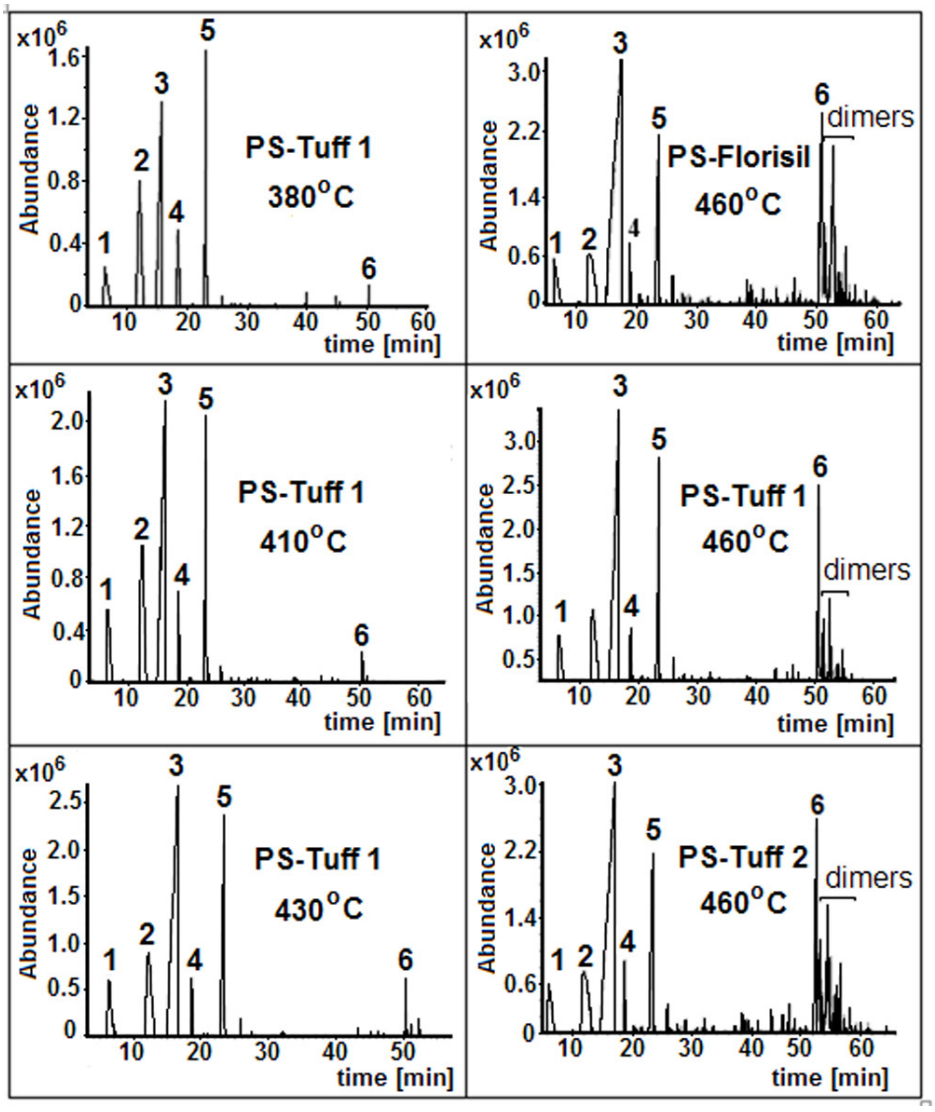


Figure 7. GC-MS chromatograms of some liquid products obtained by thermal and catalytic degradation of PS.

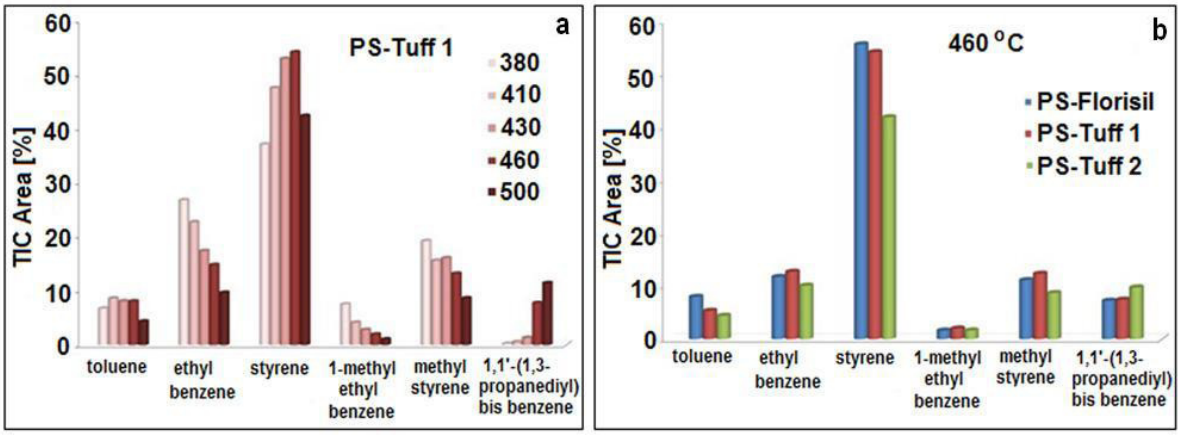


Figure 8. Distribution of compounds (TIC area, %) from liquid products obtained by thermal degradation of PS in presence of Tuff 1 catalyst.

Table 2. The assignments of absorption bands of studied liquids [39].

Group frequency (cm^{-1})	Functional group	Assignment
3081,3060,3027	C-H aromatic ring	C-H stretching
2962	methyl	ν_{asym} (CH_3), C-H asymmetric stretching
2927	methylene	ν_{asym} (CH_2), C-H asymmetric stretching
2869	methyl	ν_{sym} (CH_3), C-H symmetric stretching
1629	vinyl	ν (C=C), stretching (origin CH=CH)
1602;1494	aromatic ring	aromatic ring
1450	C-CH_3	δ_{as} C-CH_3 asymmetric bending
1081;1020	vinyl	C-H in plane bending
991; 908	vinyl	C-H out-of-plane bending
730	aromatic ring	aromatic ring rocking
777;694	mono substituted aromatic ring	C-H out-of-plane bending of aromatic ring

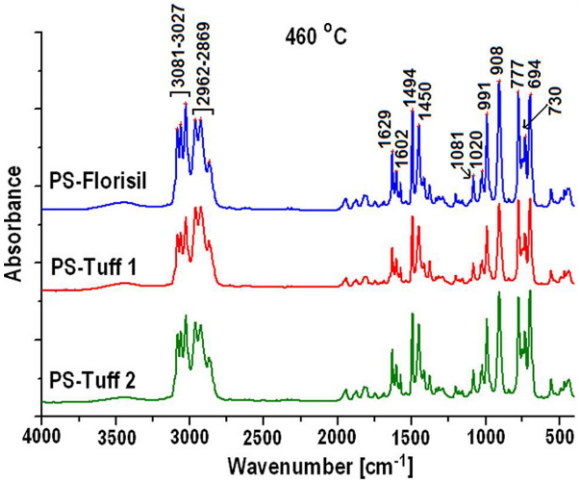


Figure 9. FTIR spectra of liquid products obtained by thermal degradation at 460°C of PS in presence of studied catalysts.

catalyst. The textural properties of Tuff 1 catalyst, like the surface area of 138.31 m^2 g^{-1} or average pore diameter of 95 Å, have an important influence on product distribution.

The presence of Tuff 2 catalyst in thermal degradation at 460°C of polystyrene waste determined the largest quantity obtained of 1,1'–(1,3-propanediyl)bis benzene of 9.74% as well as styrene monomer of 41.87%.

3.3.2. FTIR analysis

FTIR technique is widely used to interpret the molecular characteristics and structure of organic compounds and are able to quickly discern different bond vibration modes of molecules [39].

FTIR spectra of all liquid products studied show the same absorption bands that are specific to main hydrocarbon compounds. Thus, in Fig. 9 are presented the selected FTIR spectra of the liquid product obtained from the thermal degradation at 460°C of PS in presence of studied catalysts.

The main absorption bands and the type of the characteristic vibrations (stretching, bending, rocking) of the functional groups of the liquid products obtained from thermal and catalytic degradation of PS are presented in Table 2.

In FTIR spectra of liquid products, it can be observed that three bands at 3081, 3060 and 3027 cm^{-1} were assigned to the vibration of C-H bond in the aromatic ring. In addition, there are strong bands present in the region of 675–900 cm^{-1} that confirm the presence of aromatic compounds. The presence of methyl groups are indicated by the bands from 2962 and 2869 cm^{-1} that correspond to the asymmetric and symmetric stretching vibrations of C-H bond. The asymmetric stretching vibration of C-H bond in the methylene group can be observed at 2927 cm^{-1}. The intense absorption band from 1629 cm^{-1} may be assigned to the characteristic vibrational mode of C=C bond (origin CH=CH), and those of 991 and 908 cm^{-1} are attributed to the C-H out-of-plane bending vibrations corresponding to the vinyl group. The band at 1450 cm^{-1} can be assigned to asymmetric bending vibration of C-CH_3 group. The aliphatic functional groups observed in the FTIR spectra indicate that these aliphatic groups are probably present as alkyl groups attached to the aromatic rings.

The FTIR results of the liquid products obtained from the thermal degradation of PS in presence of studied catalyst are in a good agreement with those obtained by GC-MS analysis.

4. Conclusions

Thermal and catalytic degradation of polystyrene waste over two different samples of natural zeolitic volcanic tuff catalysts comparative with Florisil catalyst has been carried out in order to establish the conversion degree into styrene monomer.

The influences of the temperature and the type of catalysts on the yields and the distribution of end-products obtained by thermal and catalytic degradation of PS have been studied. The maximum yields of liquid products were obtained at 460°C degradation temperature and were calculated between 83.45% and 90.11%.

The GC-MS analyses showed that the liquid products contain mainly styrene monomer (up to 55.62%), toluene, ethylbenzene, 1-methylethylbenzene, α-methylstyrene and 1,1'–(1,3-propanediyl)bis benzene.

The FTIR spectra of liquid products of thermal and catalytic degradation of PS indicated the specific vibration bands of the functional groups methyl, methylene, aromatic ring, vinyl double bond and C-CH_3 bond from the branched structure of the compounds from liquid products. The amounts of styrene monomer obtained were influenced by structural and textural properties of studied catalyst. The most efficient catalyst in the thermal degradation of polystyrene waste was found in Florisil. Also natural volcanic tuff is an efficient and cheap catalyst for degradation of polystyrene waste and can produce a higher quantity of styrene monomer (54.16%).

The results obtained show that the thermal degradation process of polystyrene waste in presence of natural volcanic tuff and Florisil catalysts can be used as a recycling method of polystyrene waste into styrene monomer.

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