Hydrogenative pyrolysis of waste tires

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Abstract

Hydrogenative pyrolysis of waste tires, using 1,2,3,4-tetrahydronaphthalene (tetralin) as a model hydrogen donor, was carried out in a stirred batch reactor under a nitrogen atmosphere. The temperature, kept constant during each run, was varied in the range 260–430°C. Either tire granules ($\approx 2\,mm$ size) or tire particles (size less than $500\,\mu m$) were used.

Liquid-phase and gas-phase samples were withdrawn at regular intervals during each reaction run. The gas samples and the gas present in the reactor at the end of each run were collected in a bag and analyzed. The analysis of samples was performed by gas-chromatography, usually with flame ionization detection (FID), although a mass spectrometry detector (MSD) was used for initial identification of the reaction products. More than 150 major chemical compounds in the gas and liquid phases, produced by the tire depolymerization, were detected and their concentrations were evaluated as a function of the reaction time. Liquid samples were also analyzed with a thermogravimetric (TG) balance to ascertain the presence of compounds having such high boiling points as to be undetectable by gas-chromatography. In order to check if the compounds detected represented all the tire pyrolysis products a mass balance was performed.

The results of the investigation permit the identification of the most convenient operating conditions for obtaining complete depolymerization. Correspondingly, the recovery of chemicals achievable was determined.

Keywords: Depolymerization; Gas-chromatography; Hydrogenative pyrolysis; Tetralin hydrogen donor; Thermogravimetric analysis; Waste tires

1. Introduction

The accumulation of large quantities of used tires has become a major environmental problem. Environmental legislation prohibits their incineration unless an adequate means

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of preventing air pollution is provided. In fact, large quantities of particulate matter, condensed polyaromatic hydrocarbons, and sulfur and nitrogen oxides are produced during the combustion of waste tires. Pollution abatement equipment can be very effective but also expensive, thus calling into question the economic viability of incineration.

The most common method of disposal of waste tires is their dumping in open storage or in landfill sites. However, the physical properties of tires give rise to problems when landfill disposal is used. Tires have high resistance to biodegradation, and therefore do not decompose and will simply increase in volume making the site difficult to redevelop [1]. The low bulk density of tires leaves the ground soft and spongy and hence incapable of supporting the weight of dumping trucks. Tires tend to resurface after burial [2] thus making the disposal areas ideal habitats for rats, mosquitoes and flies. Moreover, landfill disposal ignores the potential economic recovery of energy and chemical materials from waste tires. In fact, tires have a high calorific value (6800–7600 kcal kg^{-1}) and are constituted of many chemicals and materials some of which are valuable: elastomer (41–48 wt%), carbon black (21–28 wt%), steel (10–25 wt%), fabric belts (3–6 wt%), extender oil and vulcanization process initiators and accelerators (9–12 wt%).

Pyrolysis is a possible alternative to thermal incineration and to landfill for the disposal of waste tires. By pyrolysis, waste tires become a potential source of fuels and recovery products. Moreover the pyrolysis disposal method has the advantage that emissions into the atmosphere are drastically reduced.

Three possible pyrolysis techniques have been investigated by several authors for the disposal of tires. They are: gas–solid pyrolysis [3–5], vacuum pyrolysis [6], and liquid–solid pyrolysis [7]. Reaction temperatures reported are: 450–500°C [3–5]; 450°C [6] and 400–500°C [7]. Generally the distribution of pyrolysis products into gas, liquid, and solid phases are reported. The gas phase consists mainly of aliphatic hydrocarbons, hydrogen and hydrogen sulfide; the liquid phase contains primarily aromatic hydrocarbons; and the solid residue consists of steel, carbon black and unreacted organic matter (char). Evaluation of the literature on product composition gives the following results (expressed as weight percentage of steel-free tires): gas phase 14% [3], 2% [6]; liquid phase 44% [3], 61–63% [6]; solid phase 43% [3], 34–36% [6]. The gaseous and liquid products could be recovered as fuel; the liquid could also be added to petroleum refinery feedstocks. The carbon residue could be used as smokeless fuel, as carbon black or, as suggested in the literature, as activated carbon [1,4,8]. In any case, the success of a recovery process for waste tires depends strongly on the quality of the by-products and their economic value.

To provide a new approach to the recovery of hydrocarbons from waste tires, we have investigated the liquid–solid pyrolysis process carried out in the presence of a hydrogen donor. This process has proved very effective in the technology of coal liquefaction. In principle, the depolymerization by pyrolysis of the polymeric matrix of tires takes place in a similar way to the depolymerization of the polymeric matrix of coal. Therefore a process which has proved effective for coal liquefaction could also prove to be effective for the depolymerization of tires.

The presence of a hydrogen donor (any hydroaromatic compound) during the pyrolysis of a polymeric material causes rapid saturation of the bonds, which are

thermally broken, thus reducing drastically the recombination of free radicals and coking reactions. Therefore, the use of hydrogenative pyrolysis for the depolymerization of tires could provide the following advantages in comparison with straight pyrolysis:

- minimization of secondary repolymerization and recondensation reactions, thus reducing the amount of char and coke;
- maximization of the yield of light hydrocarbons both in the liquid and gas phases;
- lower processing temperature;
- possibility of controlling the quality of the products with specific reference to the ratio of saturated/unsaturated compounds.

The main purpose of the investigation is to obtain as complete a picture as possible of the chemical compounds which are produced in both the liquid and gas phases during hydrogenative pyrolysis over a large temperature range. Therefore, a gas-chromatograph with capillary column and both flame ionization and mass spectrometry detectors was used. This analytical apparatus allowed us to detect about 150 chemical compounds, 100 of which were also identified. The compounds detected were classified into homogeneous groups and the concentrations of these groups were evaluated as a function of reaction time. On the basis of the concentration of the detected compounds, measured at the end of the runs, a mass balance was performed in order to check if the compounds detected represented all the pyrolysis products recovered from the loaded tire material.

2. Materials, apparatus, and experimental procedure

Steel-free tire granules with an average size of about 2 mm were provided by Eniricerche. In some runs the granules were used as received. In others they were ground and sieved and the fraction of particles with dimensions $< 500\,\mu$m was used. Grinding was carried out in the bowl of a cutting device in the presence of liquid nitrogen. Pure 1,2,3,4-tetrahydronaphthalene (99%, Aldrich) was used as a model hydrogen donor (in the following indicated as tetralin).

The reaction runs were carried out in a 300 mL autoclave with magnetic stirring, equipped with sampling lines for both the liquid and gas phases. Reaction temperature was controlled by a temperature controller. Liquid sampling was driven by the difference between the internal pressure of the reactor during a run and the external pressure. A stainless-steel sintered filter placed at the opening of the liquid sampling line, inside the autoclave, prevented loss of the solid. The gas sampling line was equipped with a condenser cooled with dry ice, a sampling port with a silicone rubber septum for syringe (Dynatech with push-button valve) sampling and finally a bag to collect all the gas produced. The sample bag (Alltech) was furnished with an on/off valve and a silicone rubber septum to allow the withdrawal of gas samples by syringe. A schematic diagram of the apparatus is shown in Fig. 1.

Two different sets of experiments were carried out in which tire granules or particles were reacted in the presence of tetralin. Besides these experiments, a blank run (tetralin without tire) was made to investigate tetralin stability and to identify the tetralin decomposition products. The experimental procedure was changed slightly depending on the set of experiments which was run. The operating temperature and pressure at which
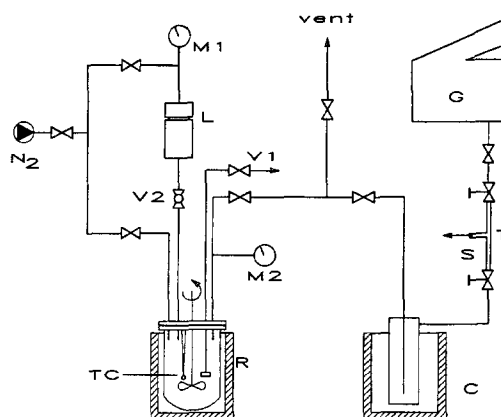
Fig. 1. Schematic diagram of the experimental apparatus: V1 = valve for the withdrawal of the liquid samples; V2 = loading globe valve; L = loader; R = stirred batch reactor; TC = thermocouple; C = dry ice condenser; T = gas phase sampling tube; S = silicone rubber septum for gas phase sampling; G = collection bag; M1 = loader manometer; M2 = reactor manometer.

the runs were performed are reported in Table 1 together with the reactor loading conditions. Nitrogen was used for pressurizing the reactor.

In the first set of experiments (runs 1, 2, and 3) tetralin and tire granules ($d \cong 2$ mm) were loaded into the reactor and its head space was flushed with nitrogen to remove the air. The reactor was then pressurized with nitrogen to the pressure value set for the run (see Table 1) and the stirring commenced. Next the reaction mixture was heated from ambient temperature to the set temperature. The time at which the reaction temperature was reached was taken as the zero time of the reaction run. From this time the temperature and the pressure were kept constant and periodic sampling of both the liquid and the gas phases commenced. Liquid phase samples, averaging about 1 mL each, were collected. The sampling line was flushed before each sampling (line volume ≈ flush volume ≈ 2 mL). Sampling was more frequent initially, when the rates of the phenom-

Table 1
Feed and operating conditions

Run	T (°C)	p (bar)	W_t (g)	d (mm)	W_d (g)	External loader	$f \times 100$ (g g^{-1})	Gas and liquid sampling
1	380	50	10.0	2	150.0	No	6.7	Yes
2	410	100	25.0	2	150.0	No	16.7	Yes
3	420	30	25.0	2	150.0	No	16.7	Yes
4	260	50	5.87	≤ 0.5	84.9	Yes	6.9	Yes
5	345	50	6.70	≤ 0.5	99.0	Yes	6.7	Yes
6	380	50	6.29	≤ 0.5	105.8	Yes	5.9	Yes
7	393	50	6.82	≤ 0.5	91.0	Yes	7.5	Yes
8	430	50	4.92	≤ 0.5	91.8	Yes	5.4	Yes
9	393	50	6.15	2	87.4	No	7.0	No
Blank	393	50	–	–	97.8	Yes	–	Gas

ena of interest were larger. Sampling of the liquid phase disturbed the temperature and pressure level in the reactor to a limited extent. As with liquid sampling, the gas line was washed before a gas sample was taken allowing the fresh gas to remove the components from the previous sampling, forcing them into the collection bag. After each gas-phase sampling the pressure in the reactor diminished by about 5 bar. The pressure was restored by introduction of nitrogen. A minor effect was observed on the reactor temperature which remained practically constant. At the end of the run the reactor was depressurized by venting the gaseous contents into the collection bag via the gas sampling line. In none of the runs (except run 3) were condensables present in the condenser. Maybe the low pressure (30 bar) adopted in run 3 caused the spillage and condensation of a large amount of tetralin.

The experimental procedure followed for the first set of experiments has the advantage of allowing the loading of the reactor with full-size tire granules and in any weight ratio with tetralin. In fact, experiments with feed ratios as large as 0.167 (g tire g^{-1} tetralin) were accomplished. Large feed ratios are convenient. The larger the feed ratio, the higher is the concentration of pyrolysis products at any time in the reacting mixture. On the other hand, however, with this procedure the full reaction run is not isothermal due to the preheating period of the reactor. During preheating uncontrolled reaction takes place.

The second set of experiments (runs 4-8) was made following a different procedure in order to avoid the inconvenience of the preheating period. The reactor was equipped with an external loader (see Fig. 1) having a volume of about 70 mL. A slurry of the weighed tire particles ($d \leq 500 \mu$m) in part (about 50 g) of the tetralin required for the run was put into the loader which was then assembled and connected to the reactor by a globe valve. At this time the heating of the reactor, previously loaded with the remainder of the tetralin (about 50 g), was started. When the required temperature was reached the loader was pressurized with nitrogen and the slurry (tetralin/tire particles) was allowed to enter the reactor quickly by opening the globe valve. This is taken as the zero time of the reaction run. The instantaneous injection of the liquid suspension contained in the loader caused a thermal transient. Thereafter the set temperature was again reached in about 2-3 min. The pressure level for the runs was set as low as possible. The pressure was set at 50 atm to avoid the spillage and the condensation of a large amount of tetralin (as in run 3 when $P = 30$ atm) during the gas sampling, and to achieve efficient loading. Then samples were collected as described previously. With this procedure we could only load tire particles. The granules were much too large to be loaded through the globe valve. Furthermore, due to the size of our reactor it was not possible to realize feed ratios larger than 0.07 (g tire g^{-1} tetralin, see Table 1). In fact, to restore the reactor temperature quickly after loading of the cool slurry, the weight of tetralin loaded in the reactor had to be about equal to the weight of the slurry in the loader. Consequently, the loadable weight of tire particles was limited so as to avoid the formation of too thick a slurry which would have not easily entered the reactor on opening the globe valve.

Finally run 9 was made according to the procedures described above but no samples were collected during the run. In this way any loss of material due to the sampling procedure was avoided and it was possible to check the overall material balance of the process.

More detailed information on the apparatus and the procedure for performing the pyrolysis runs is given by Garufi [9] and Smith [10].

3. Chemical analysis of samples

Gas and liquid samples were analyzed with an HP-5890A gas-chromatograph equipped with a flame ionization detector (FID).

For the analysis of the liquid samples the gas-chromatograph was equipped with an HP-Ultra2 (5% phenyl polydimethylsiloxane) column ($l = 50$ m, i.d. = 0.2 mm). The operating conditions were: injector pressure 33 psig; injector temperature 320°C; detector temperature 330°C. The oven temperature program was: 15 min at 130°C; ramp rate 10° min^{-1}; 30 min at 280°C.

For the analysis of the gas samples the same gas-chromatograph was equipped with a HP-PLOT Al_2O_3/KCl column ($l = 50$ m, i.d. = 0.32 mm). The operating conditions were: injector pressure 15 psig; injector temperature 190°C; detector temperature 200°C. The oven temperature program was: 2.5 min at 30°C; ramp rate 5° min^{-1}; 10.5 min at 190°C.

The same gas-chromatograph, using the same columns but with an HP-5970B mass spectrometer detector (MSD), was utilized to identify some key components in both phases.

The identification of the key components in the gas phase was checked and completed by analyzing standard mixtures (100 ppm in helium; Scott Specialty Gases Inc.) of C_1–C_6 n-paraffins and C_2–C_6 olefins. The same mixtures were also utilized to determine GC response factors (area %/weight %).

The identification of the most abundant components in the liquid phase was checked by comparing retention times with those of standards. For the liquid phase, the response factor was assumed equal to unity for all the hydrocarbon compounds detected [11]; i.e., for each compound, the percent chromatographic area on the chromatographic report was assumed to be equal to the weight percent concentration.

The nonhydrocarbon gas in the gas phase was analyzed by GC (HP 5700A) coupled with a thermal conductivity detector (TCD).

The liquid samples collected at the beginning and end of runs 4–6 and 8 were also analyzed by means of a thermogravimetric balance (Perkin–Elmer TGS-2 thermogravimetric system) to evaluate the presence of compounds with such high boiling points as to be undetectable by the GC apparatus. The samples were centrifuged and the liquid phase was analyzed. The TG operating conditions were: nitrogen flowrate 20 mL min^{-1}; heating rate 40° min^{-1}; initial temperature 50°C; final temperature 510°C; volume of sample $\approx$ 10 μL; mass of sample $\approx$ 11.5 mg. The same analysis was performed on the residual liquid phase at the end of run 9, which was carried out without sampling.

The solid residue was collected from the reactor, washed with tetrahydrofuran, filtered and then weighed. The recovered tetrahydrofuran was analyzed by GC, using the same procedure adopted for the liquid samples, to evaluate the amount of pyrolysis products in the solid residue which were soluble in tetrahydrofuran.

Further details of the analytical methodology are described by Garufi [9] and Smith [10].

4. Results of chemical analysis and discussion

In the following, the analytical results obtained for both the gas and liquid phases are discussed. Attention is focused on runs 4–8 for which the thermal transients were minimized by the use of the external loader.

4.1. Gas phase

The results from analyses of the gas phase present in the collection bag at the end of each run are reported in Figs. 2 and 3. The gas phase was principally constituted of nitrogen (used to pressurize the reactor), the products of tire hydrogenative pyrolysis (hydrocarbons, carbon monoxide and dioxide), and hydrogen from tetralin dehydrogena-
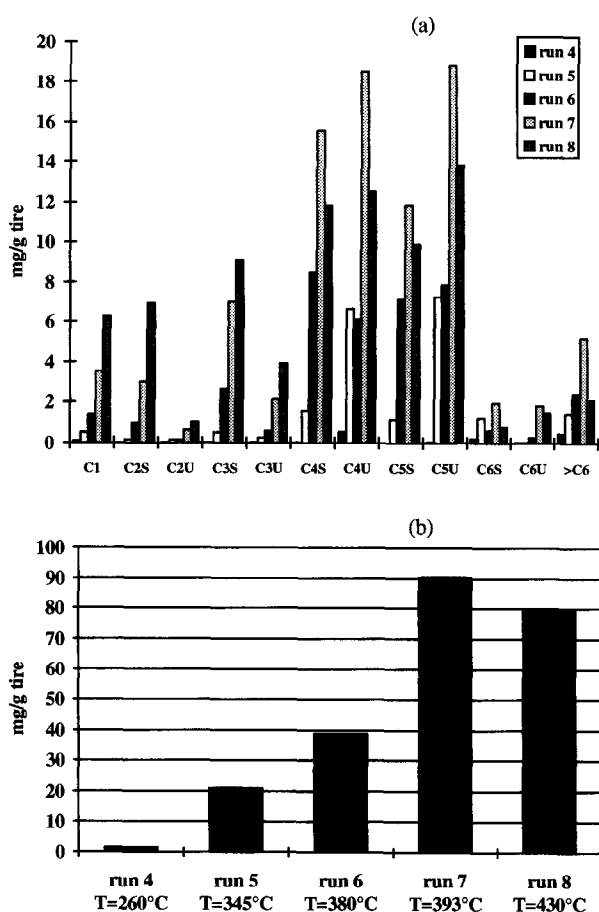

Fig. 2. (a) Classification of gaseous hydrocarbons formed by tire conversion at the reaction temperatures investigated. (b) Amounts of gaseous hydrocarbons formed by tire conversion at the reaction temperatures investigated.
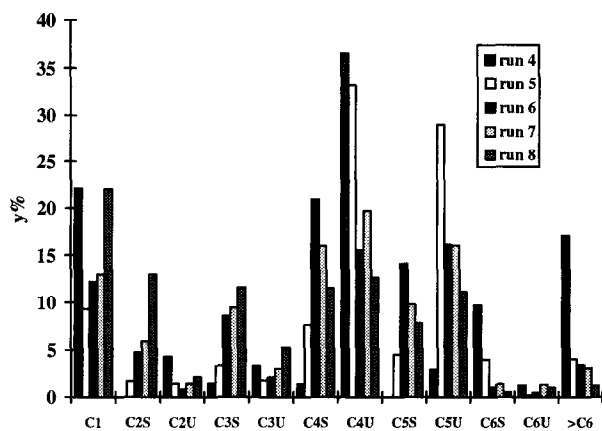
Fig. 3. Molar percentage of gaseous hydrocarbons classified into groups versus reaction temperature. Molar percentage is based on the total moles of hydrocarbons in the gas phase.

tion. The contribution of tetralin to the production of gaseous hydrocarbons can be neglected. In fact, the amount of gaseous hydrocarbons produced in the blank run (only tetralin loaded in the reactor) is $\approx 6.5\%$ of that produced in run 7 which was carried out at the same temperature ($T = 393°C$). Concentrations are reported as $mg\,g^{-1}$ of loaded tire in Fig. 2 and as molar fraction y ($mol\,mol^{-1}$ hydrocarbons) in Fig. 3.

More than 60 hydrocarbon pyrolysis products were detected in the gas phase. The most abundant hydrocarbons have been identified and are listed in Table 2. At any rate, the hydrocarbons which have not been identified are only present in small concentrations. In the same table, the molar percentages of the identified hydrocarbons (based on total hydrocarbons), as measured in the gas collection bag at the end of runs 5–8, are also reported. Run 4 ($T = 260°C$) is not considered in Table 2 inasmuch as very low concentration levels were obtained in the gas phase, due to the low reaction rate. Therefore the calculated relative concentrations could be affected by large error.

To simplify the analysis, all hydrocarbons detected have been classified on the basis of the number of carbon atoms and of the saturation of the C–C bonds. The following groups are defined: C_1, C_{2S}, C_{2U}, C_{3S}, C_{3U}, C_{4S}, C_{4U}, C_{5S}, C_{5U}, C_{6S}, and C_{6U} (e.g., the C_{4S} group contains all saturated compounds with four carbon atoms, while the C_{4U} group contains all unsaturated compounds with four carbon atoms). Hydrocarbons with more than six carbon atoms are present in very small amounts. They are grouped together and the corresponding group named as $> C_6$

The amounts ($mg\,g^{-1}$ of loaded tires) of gaseous hydrocarbons, detected at the end of runs 4–8 in the collection bag, are reported in Fig. 2(a) and (b). Fig. 2(a) refers to the single groups defined above. Fig. 2(b) refers to the overall production of hydrocarbons. Inspection of Fig. 2(a) and (b) indicates that:
- no significant production of gaseous hydrocarbons takes places at $T = 260°C$ (run 4);
- only compounds of groups C_{4U} and C_{5U} are produced in important amounts at $T = 345°C$ (run 5);

Table 2
Most abundant hydrocarbons present in the collection bag at the end of selected runs, in order of elution time. Relative concentration is molar percentage based on hydrocarbon fraction

Compound	Relative concentration (mol%)				Elution times (min)
	Run 5	Run 6	Run 7	Run 8	
Methane	9.31	12.23	13.00	22.05	3.63
Ethane	1.65	4.68	5.89	13.02	4.46
Ethylene	1.40	0.81	1.38	2.08	5.54
Propane	3.37	8.56	9.45	11.66	7.97
Propylene	1.74	2.05	3.03	5.27	12.02
Isobutane	6.75	17.77	12.66	7.72	14.46
n-Butane	0.87	3.12	3.30	3.82	15.34
2-Butene, trans	1.62	2.04	1.77	2.17	19.18
1-Butene	0.85	0.97	1.10	1.40	19.50
Isobutylene	29.20	11.10	15.57	7.46	20.05
2-Butene, cis	1.13	1.42	1.26	1.50	20.78
2,2-Dimethylpropane	0.62	0.89	0.97	0.61	21.26
2-Methylbutane	3.68	12.62	7.79	6.39	22.64
n-Pentane	0.18	0.55	0.89	0.68	23.48
1,3-Butadiene	0.36	0.04	0.17	0.15	24.09
3-Methyl-1-butene	0.24	0.37	0.32	0.32	26.18
2-Methyl-2-butene	19.89	9.83	10.14	6.65	26.69
Ethylcyclopropane	n.i. [a]	0.20	0.24	0.22	26.93
1,2-Dimethylcyclopropane, cis	6.87	4.45	3.74	2.85	27.14
2-Methyl-1-pentene	0.12	0.26	0.43	0.28	29.38
2-Methylpentane	0.25	0.50	0.57	0.29	30.13
3-Methylpentane	0.17	0.43	0.50	0.24	30.31
Methylpentene	3.58	0.20	0.80	0.67	30.87
n-Hexane	n.i.	0.11	0.29	n.i.	31.02

[a] Not identified in this run.

- significant production of hydrocarbons takes place at $T > 345°C$ (runs 6–8); and
- the amount of compounds in groups C_{2U}, C_{3U}, C_6, and $> C_6$ is always very low at any reaction temperature.

In order to highlight the influence of temperature on the composition of the hydrocarbon fraction, the concentration of each group in the collection bag at the end of the run, expressed as molar percent (based on total hydrocarbons), is reported in Fig. 3. Inspection of this figure shows that the temperature influences both the degree of saturation of C–C bonds and the mean molecular weight. In fact, as the reaction temperature rises:

- the concentration of the unsaturated compounds markedly decreases (see C_{4U} and C_{5U}) while the concentration of saturated compounds increases (see C_{2S} and C_{3S}); and
- the concentration of the heaviest gaseous hydrocarbons markedly decreases (see C_4, C_5, C_6, and $> C_6$) while the concentration of the lightest increases (see C_1, C_2, and C_3).

Fig. 3b shows, as an example, the molecular weight distribution of hydrocarbons in

Table 3
Percent volume of nonhydrocarbon compounds in the collection bag at the end of selected runs

Run	N_2 (V%)	O_2 (V%)	H_2 (V%)	CO (V%)	CO_2 (V%)
5	91.26	1.71	< 2	< 0.10	0.12
6	83.56	8.90	< 2	< 0.10	0.21
8	83.65	3.06	8.53	< 0.10	0.18
9	83.50	0.90	4.44	0.22	0.20
Blank	86.38	0.60	4.59	< 0.10	0.08

the gas phase for run 7 (T = 345°C). It can be observed that the molecular percentage of C_4 and C_5 hydrocarbons is more than 60% of the total hydrocarbons produced.

The effect of sampling of the gas phase present in the reactor on the relative concentrations reported in Figs. 2 and 3 is minimal. In fact the volume collected after the sampling operations was very small relative to the volume present in the collecting bag at the end of each run when the reactor was depressurized and all the gas phase collected. The gas phase concentration data points versus time obtained from the gas samples taken at various times during the run are reported elsewhere [9]. They are being used for the kinetic analysis of the process which will be discussed in another paper to be published separately.

The concentrations of gases other than hydrocarbons, identified by GC–TCD analysis, are reported in Table 3 for runs 5, 6, 8, 9, and the blank run. H_2S and H_2O could not be identified by our GC–TCD apparatus. The threshold level for H_2 was about 2% by volume.

4.2. Liquid phase GC analysis

The compounds in the liquid phase samples, as identified by GC–MS, are reported in Table 4. The range of compounds detectable by our analytical apparatus includes hydrocarbons with a maximum molecular weight of about 300 [11]. Routine analyses were accomplished by GC–FID in order to determine the concentrations of the detected compounds.

Due to the large number of compounds a classification procedure was necessary. In order to find a classification criterion, the chromatograms of the tire pyrolysis runs were compared with those of the pyrolysis of pure tetralin (blank run and results of previous work [11]). The following groups were then defined:

- 'Low molecular weight compounds' (**LMWC**); eluted before 2,3-dihydroindene (indan); MW < 118;
- 'Medium molecular weight compounds' (**MMWC**); eluted between indan and naphthalene, both included; $118 \le MW < 135$;
- 'High molecular weight compounds' (**HMWC**); eluted after naphthalene; $135 \le MW \le 300$.

'Low molecular weight compounds'. More than 40 pyrolysis products belong to this group. They are linear and cyclic hydrocarbons with 4 to 7 carbon atoms, both saturated and unsaturated, and alkylbenzenes. In the case of tetralin pyrolysis few compounds

with retention time less than indan were detected [11,12].

Comparing the chromatograms of run 7 ($T = 393°C$) with those of the blank run at the same temperature, we observe that the contribution of the pyrolysis of tetralin to the yield of the group is minor (< 10 wt% at the end of the run: $t = 240$ min). In contrast, at higher temperatures the contribution of tetralin pyrolysis becomes more significant. In fact, by comparing the chromatograms of run 8 ($T = 430°C$) with those of tetralin pyrolysis at the same temperature [11] we observe that the contribution of tetralin pyrolysis rises to 50% wt.

Therefore the LMWC are assumed to be produced entirely by tire pyrolysis at reaction temperatures lower than 380°C (runs 4–6). At higher temperatures (runs 7–8) the contribution of tetralin pyrolysis products must be taken into account and the net concentration of tire pyrolysis products is evaluated by subtracting the contribution from tetralin pyrolysis. The conversion of the tire to LMWC ($g\,g^{-1}$ of loaded tire) at the end of the runs 4–8 is reported in Fig. 4 versus the reaction temperature. Fig. 4 indicates that the production of the LMWC becomes significant at temperatures higher than 350°C.

'Medium molecular weight compounds'. Compounds belonging to this group include tetralin and the principal reaction products of the pyrolysis of tetralin; i.e., naphthalene, 1-methylindan and *n*-butylbenzene. However, by comparing the chromatograms of runs 7 and 8 with the blank run and with the results of the previous investigation on tetralin pyrolysis [11] we observe that a significant contribution to the yield of *n*-butylbenzene is due to tire pyrolysis. As a matter of fact, the polymeric structure of the tire contains aromatic rings linked by aliphatic chains. Therefore, *n*-butylbenzene can be a reaction product of the pyrolysis of tire as well. The net concentration of *n*-butylbenzene is evaluated by subtracting the contribution from tetralin pyrolysis.

'High molecular weight compounds'. Compounds belonging to this group have molecular weights in the range 134–300. The upper limit was fixed by a preliminary analysis using standard compounds and represents the molecular weight of the heaviest compound elutable by GC. Furthermore, the same analysis showed that compounds with MW smaller than 200 have GC response factors (area%/weight%) of about 1 while compounds with MW in the range 200–300 have response factors which decrease from 1 to 0.2. Because of the high number of pyrolysis products, the majority of which have MW < 200, a response factor of 1 was assumed for all the compounds detected. In conclusion, compounds with MW up to 300 are detectable, however, their quantitative analysis is reliable only up to MW = 200.

The contribution of tetralin pyrolysis to the group is evaluated to be 20 wt% at $T = 393°C$ and 34 wt% at 430°C. Therefore, for runs 7 and 8, the net concentration of HMWC is evaluated by subtracting the contribution from the tetralin pyrolysis. At lower temperatures (runs 4–6) the contribution from tetralin pyrolysis is neglected.

4.3. Liquid phase analysis by thermogravimetric analysis

The possible presence of compounds in the liquid phase not elutable by GC was checked by thermogravimetric analyses. The results of these analyses are reported in Table 5 as residual weight% on the TG balance at selected balance temperatures T_b.

Table 4
Compounds identified in the liquid phase by GC–MS with corresponding elution time and percentage of identification

Number	Compound	Elution time (min)	Percentage of identification by GC–MS
1	Isobutane	3.60	47
2	2-Butene [b]	–	–
3	Isopentane	3.66	76
4	n-Pentane	3.68	47
5	trans-1,2-Dimenthylcyclopropane	3.69	91
6	3-Methyl-1-butene	3.71	86
7	2-Methyl-2-butene	3.71	–
8	cis-1,2-Dimethylcyclopropane	3.71	58
9	2-Methylpentane	3.76	80
10	3-Methylpentane	3.79	78
11	2,4-Dimethylpentane	3.86	64
12	5-Methyl-1-hexene	3.90	78
13	1,2-Dimethyl-3-methylenecyclopropane	3.94	87
14	3-Ethylpentane	3.97	74
15	3-Methylhexane	4.02	64
16	trans-1,2-Dimethylcyclopentane	4.03	64
17	2-Heptene	4.05	81
18	3-Methyl-1-hexene	4.05	72
19	cis-1,2-Dimethylcyclopentane	4.05	62
20	3,3-Dimethyl-1,4-pentadiene	4.12	72
21	1,5-Dimethylcyclopentene	4.13	76
22	Methylcyclohexane	4.18	80
23	4,4-Dimethylcyclopentene	4.25	72
24	3-Methylcyclohexene	4.26	81
25	Methylbenzene [a]	4.36	95
26	1,4-Dimethylcyclohexane	4.40	90
27	1-Ethyl-3-methylcyclopentane	4.45	90
28	trans-1,2-Dimethylcyclohexane	4.56	81
29	Ethylcyclohexane	4.74	72
30	Ethylbenzene [a]	4.91	90
31	1,3-Dimethylbenzene	4.93	72
32	1,2-Dimethylbenzene	5.21	90
33	1-Methylethylbenzene	5.39	72
34	Propylbenzene [a]	–	–
35	1,2,3-Trimethylbenzene	5.00	59
36	1-Ethyl-4-methylbenzene	6.18	53
37	cis-1-Methyl-4-(1-methylethyl)cyclohexane	6.26	72

Inspection of Table 5 shows that samples collected at the end of tire pyrolysis runs are not completely vaporized at $T_b = 320°C$, which is the GC injector temperature. At $T_b = 510°C$ a residual weight is still present on the balance. This is an indication that compounds having such high boiling points as to be undetectable by our GC apparatus, are produced. These compounds are exclusively due to the pyrolysis of tire. In fact, the sample collected at the end of the blank run does not show any residual weight at $T = 320°C$. It may be assumed that the residual weight on the TG balance at $T_b = 320°C$

Table 4 (continued)

Number	Compound	Elution time (min)	Percentage of identification by GC–MS
38	4-Methyl-1-(1-methylethyl)cyclohexane [b]	–	–
39	2,4,4-Trimethyl-2-pentene	6.41	87
40	2-Ethyl-1,3-dimethylbenzene	6.81	68
41	1-Methyl-3-(1-methylethyl)benzene	6.82	87
42	1-Methyl-2-(1-methylethyl)benzene	6.83	91
43	2-Ethyl-1,3-dimethylbenzene	6.98	90
44	4-Ethyl-1,2-dimethylbenzene	7.00	64
45	Indan [a]	–	–
46	Butylbenzene [a]	7.54	100
47	1-Methylindan [a]	8.47	100
48	1-Methyl-4-propylbenzene [b]	–	–
49	4-Ethenyl-1,2-dimethylbenzene [b]	–	–
50	(2-Methyl-2-propenyl)benzene [b]	–	–
51	Decahydronaphthalene [b]	–	–
52	1,2,3,4-Tetrahydronaphthalene (tetralin) [a]	12.1	100
53	Naphthalene [a]	13.0	100
54	1-Methyl-1,2,3,4-tetrahydronaphthalene [b]	–	–
55	6-Methyl-1,2,3,4-tetrahydronaphthalene [b]	–	–
56	1-Methylnaphthalene	18.4	80
57	2-Methylnaphthalene [b]	–	–
58	5-Ethyl-1,2,3,4-tetrahydronaphthalene	18.6	72
59	3,4-Dihydro-1(2H)-naphthalene [b]	–	–
60	2-Ethylnaphthalene [b]	–	–
61	2,3,5-Trimethyldecane [b]	–	–
62	1,7-Dimethylnaphthalene [b]	–	–
63	Undecane [b]	–	–
64	1,2-Dimethylnaphthalene [b]	–	–
65	Pentadecane	23.1	98
66	6-(1,1-Dimethylethyl)-1,2,3,4-tetra-hydronaphthalene	23.2	93
67	2-(1,1-Dimethylethyl)-1,2,3,4-tetra-hydronaphthalene	23.4	86
68	1,1-Dimethylindan	24.1	72
69	Hexadecane [a]	25.3	91
70	Heptadecane	27.0	93
71	Docosane	31.0	98
72	1-Octyl-1,2,3,4-tetrahydronaphthalene	37.1	72
73	1,2,3,7,8,9-Hexahydroperylene	37.5	83
74	1′,2′,3′,4′,5,6,7,8-Octahydro-1,2′-binaphthalene	38.2	80

[a] Compounds identified also by analysis of standards mixtures by GC–FID.

[b] Less abundant compounds identified by analysis with a different GC–MS apparatus.

is a measure of the amount of compounds not detectable by GC. In the following these compounds will be abbreviated to **VHMWC** (very high molecular weight compounds). With reference to the previously defined HMWC, the VHMWC are assumed to have MW > 300.

Considering the runs carried out at reaction temperatures larger than 260°C, it is interesting to note (see Table 5) that the VHMWC are present in larger concentrations at
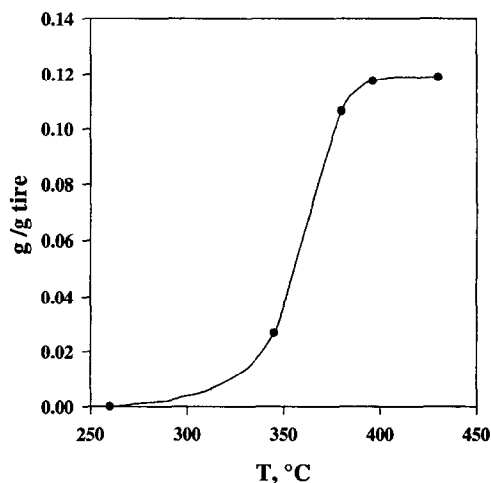
Fig. 4. Tire conversion to LMWC in the liquid phase at the end of each run versus reaction temperature.

the beginning of the runs ($t_s = 1$ min) and that their concentration decreases as the reaction proceeds. Furthermore, these compounds have a larger molecular weight at the beginning of the run. In fact inspection of Table 5 (with reference to runs at $T = 380°C$ and $T = 430°C$) shows that the samples at $t_S = 1$ min have a content of about 3% of these compounds which vaporize between 320 and 510°C. In contrast, at the end of the pyrolysis run ($t_S = 240$ min) the content is reduced to about 0.1%. These considerations let us conclude that the mechanism of tire depolymerization includes a pattern in which large fragments are detached from the polymeric matrix of the rubber and are then efficiently fragmented to lighter hydrocarbons as the pyrolysis proceeds. An opposite behavior is shown at a reaction temperature of 260°C; i.e., the concentration of the VHMWC increases with reaction time. This can be explained considering that all

Table 5

Mass remaining on the TG balance at selected temperatures. Data are expressed as wt% of loaded liquid samples. Samples are those collected at the beginning and/or at the end of runs

Run	T (°C)	t_S (min)	wt% versus T_b (°C)						
			$T_b = 170$	$T_b = 180$	$T_b = 190$	$T_b = 200$	$T_b = 320$	$T_b = 400$	$T_b = 510$
4	260	1	25.09	5.63	1.79	1.57	0.99	0.42	0.14
4	260	240	29.73	11.02	4.29	3.98	3.12	1.41	0.10
5	345	1	27.37	8.95	3.97	3.77	3.16	1.60	0.26
5	345	120	18.58	4.37	2.91	2.54	0.87	0.48	0.17
6	380	1	32.30	14.62	4.28	3.92	3.36	1.68	0.45
6	380	240	16.41	2.67	1.85	1.47	0.24	0.17	0.15
8	430	1	25.07	7.17	4.32	4.01	3.01	1.41	0.31
8	430	240	6.63	1.09	0.68	0.43	0.10	0.07	0.05
9	393	240	36.66	20.14	3.23	1.67	0.16	0.22	0.084
Blank	393	240	20.38	2.12	0.12	0.09	0	0	0

reactions are much slower at this temperature. In fact at 260°C the overall pyrolysis does not occur to any great extent.

Moreover, by subtracting the residual weights at $T_b = 320°C$ from those at $T_b = 190°C$ (temperature at which tetralin and naphthalene are practically evaporated) one obtains a measure, alternative to the GC determination, of the amount of HMWC at the end of each run. The comparison between the results obtained by the two methods is discussed in the 'Mass balance' section.

5. Hydrogen donated

An important indicator of the extent of the hydrogenative pyrolysis reactions is the amount of the hydrogen donated during the overall reaction. In order to evaluate this parameter we consider the following possible reaction describing very simply the hydrogenation step:

$$P_i^* + \alpha T \rightarrow P_i + \alpha N \tag{1}$$

where:

P_i^* = any hydrogenable compound included free radicals;
α = stoichiometric coefficient;
T = tetralin;
P_i = hydrogenated products of tire pyrolysis both in the gas and in the liquid phases;
N = naphthalene.

Simultaneously, tetralin undergoes dehydrogenation according to the following reaction:

$$T \rightarrow N + 2H_2 \tag{2}$$

The hydrogen produced by reaction 2 may be considered ineffective as far as the hydrogenative pyrolysis of tire is considered [13,14].

Due to reaction 2 the hydrogen donated cannot be calculated on the basis of the overall tetralin consumed or the overall naphthalene produced. Only the tetralin consumed (or the naphthalene produced) by reaction 1 must be accounted for. Therefore, the hydrogen donated to the compounds of tire pyrolysis must be expressed as proposed by Gioia and Murena [14] as:

$$H_D = \frac{4 \times \underline{C_N}}{f} \tag{3}$$

where:

H_D = grams of hydrogen donated to the tire material per gram of tire loaded, $(g\,g^{-1})$;
$\underline{C_N}$ = moles of naphthalene produced via reaction 1 per gram of solution, $(mol\,g^{-1})$;
f = feed ratio, gram of loaded tire per gram of solution, $(g\,g^{-1})$.

$\underline{C_N}$ can be evaluated by subtracting the contribution of reaction 2 to the total concentration of naphthalene measured during the experiments:

$$\underline{C_N} = C_N - C_{Npyr} \tag{4}$$

Table 6
Grams of hydrogen donated per gram of loaded tire

Run	T (°C)	$f \times 100$ (g g^{-1})	H_D (g g^{-1})
1	380	6.7	1.66×10^{-2}
2	410	16.7	2.12×10^{-2}
3	420	16.7	3.94×10^{-2}
4	260	7.6	6.64×10^{-4}
5	345	6.7	5.14×10^{-3}
6	380	5.9	1.81×10^{-2}
7	393	7.5	1.55×10^{-2}
8	430	5.4	8.16×10^{-2}
9	393	7.0	1.06×10^{-2}

where:

C_N = experimental naphthalene concentration, (mol g^{-1});
C_{Npyr} = concentration of naphthalene due to the pyrolysis of tetralin (reaction 2), (mol g^{-1}).

The kinetic constant of reaction 2 is available in the literature [13]; it is:

$$k_{p1} = 3.85 \cdot 10^8 \times e^{\frac{-163.3}{RT}} \tag{5}$$

where: $R = 8.314 \times 10^{-3}$ (kJ mol^{-1} K^{-1}) and the frequency factor k_{p1}^0 [=] min^{-1}. The concentration of naphthalene at the end of each run due to reaction 2 was then evaluated using the value of the kinetic constant k_{p1} calculated at each temperature by use of Eq. (5). This concentration was then subtracted from the naphthalene concentration experimentally measured at the end of each run. In this way C_N was calculated for each run. The values of H_D calculated by means of Eqs. (3)–(5) are reported in Table 6. Inspection of this table shows that the hydrogen donated increases markedly with temperature. Making reference to the run at 430°C it is interesting to note that the hydrogen donated has a value very close to that found in the process of coal liquefaction, which is a process very similar to that investigated in this paper. For coal liquefaction it is reported [14] that $H_D = 7.9 \times 10^{-2}$ (g g^{-1}) at $T = 430$°C.

6. Mass balance

In order to check if the compounds identified represent all the pyrolysis products recovered from the loaded tire material, a mass balance at the end of the runs was performed. The results are reported in Table 7 and represent the tire pyrolysis product distribution expressed as weight percent of the tire loaded.

The tire conversion to HMWC reported in Table 7 deserves discussion. As pointed out previously, these compounds are detected both by GC and by means of the TG balance. Inspection of Table 7 shows that different results are obtained by the two

Table 7
Tire pyrolysis product distribution and mass balance. The figures in the table are wt% of loaded tire

Phase	Tire pyrolysis products	Analytical method	Run 4 $T = 260°C$	Run 5 $T = 345°C$	Run 6 $T = 380°C$	Run 7 $T = 393°C$	Run 8 $T = 430°C$	Run 9 $T = 393°C$
S	Solid residue (THF uns.le)		58.73	39.13	39.68	35.48	33.83	34.6
L	LMWC (MW < 118)	GC–FID	0.00	2.68	10.66	11.74	11.89	14.9
L	MMWC ($118 \leq$ MW < 135)	GC–FID	0.00	0.83	4.07	3.42	22.18	2.57
L	HMWC ($135 \leq$ MW ≤ 300)	GC–FID	0.00	13.86	16.74	10.17	25.27	10.46
L	HMWC ($190 < T_b < 320$)	TG	16.90	30.10	27.10	n.a.	10.80	43.6
L	VHMWC ($T_b > 320$)	TG	45.09	12.86	4.04	n.a.	1.87	2.27
G	Gas (hydrocarbons, CO,CO_2)	GC–FID GC–TCD	0.15	2.79	4.42	9.03 [a]	9.15	2.56
	Total [b]		120.72	88.39	89.87	n.a.	89.72	100.5

[a] In run 7 the amount of CO and CO_2 is not available.
[b] Total is calculated using for the tire conversion to HMWC the results obtained by the TG.

analytical methods. This is not surprising because the two methods rely on different vaporization techniques. In the TG balance the sample is vaporized very slowly while in the GC injector the vaporization is much quicker. Therefore, some compounds may be not completely vaporized (and then detected) by GC. Moreover, some of the HMWC (particularly the heaviest) could not even be eluted by the column. Both these phenomena lead to underestimation of the amount of the HMWC evaluated by GC. On the other hand, TG analysis can also lead to error due to the fact that it is difficult to define precisely the lower limit of the TG temperature at which it may be assumed that the vaporization of the HMWC starts.

In conclusion when the average molecular weight of the HMWC group is shifted toward the upper limit (MW = 300), the efficiency of vaporization and elution in GC analysis can be low and the TG determination is more reliable. On the other hand when this average molecular weight is shifted toward the lower limit (MW = 134) the TG balance determination could be less accurate.

In order to make the mass balance internally consistent, the total in Table 7 has been calculated using, for the tire conversion to HMWC and VHMWC, the results obtained by a single analytical procedure; i.e., TG determination.

Inspection of Table 7 shows that for runs 5, 6, and 8 the mass balance approaches 90%. Run 7 is a preliminary run for which the TG analysis was not done. The results of run 9 carried out at the same temperature as run 7 but without sampling, check the mass balance exactly. Therefore, the mass missing in runs 5, 6 and 8 can be partly attributed to loss of material during the sampling operation. On the basis of the results obtained with run 9, which was carried out without sampling, the mass loss due to sampling was estimated to be about 4% of the total mass loaded in the reactor. An additional loss is due to the products washed out with tetrahydrofuran during washing of the solid residue. This loss is about 2% of the loaded tire.

Let us discuss run 4 ($T = 260°C$). First of all we observe that a large amount of tire does not react. In fact, the solid residue is about 60% of the loaded tire. Furthermore, the reaction products are very heavy and are detected exclusively by the TG balance. The total exceeds 100%. A possible explanation of this mass excess could be that tetralin adds to the heavy radicals which are produced during the pyrolysis process. This type of reaction is known to take place in the coal liquefaction process at relatively low reaction temperatures where preasphaltenes are produced [15].

7. Conclusions

The reaction products of the hydrogenative pyrolysis of tires are present in the gas, liquid, and solid phases.

The gas phase is rich in paraffins and olefins with 1 to 6 carbon atoms. By increasing the reaction temperature, the paraffin fraction increases and the mean molecular weight of the hydrocarbon mixture decreases. The investigation shows that in order to maximize the production of gaseous compounds a temperature of 400°C is sufficient.

The liquid phase products range from low molecular weight hydrocarbons (MW ≤ 118) to compounds having a much larger molecular weight (MW > 300). The concentra-

tion of these last compounds is a function of reaction time and reaction temperature. To minimize their concentration a temperature $T > 380°C$ is necessary.

The amount of the solid residue decreases with temperature. At temperatures greater than 380°C, the solid phase product consists essentially of carbon black loaded with the tire particles.

Comparing hydrogenative tire pyrolysis with gas–solid pyrolysis [3] the result is that:

- the lowest reaction temperatures can be used when a hydrogen donor is present: i.e.; 390–430°C versus 400–500°C;
- production of solid residue is minimized: i.e., 34% versus 43% (both percentages on a steel-free tire basis); and
- production of liquid phase is maximized: i.e.; 50–60% versus 44% (percentages as before).

The results reported in the present paper cannot give a definitive answer about the operating conditions to be adopted in the tire hydrogenative pyrolysis process for reaching a desired ratio of saturated to unsaturated products. This is because these classes of products were not identified separately in the liquid phase but only in the gas phase.

In conclusion, the hydrogenative pyrolysis is efficient in depolymerizing the organic matrix of the tires and in reducing the molecular weight of the large fragments which are produced in the early stage of the process. Moreover, the hydrogenative pyrolysis requires temperatures lower than those required in conventional pyrolysis processes. In fact, the investigation indicates that in the presence of a hydrogen donor the optimum pyrolysis temperature ranges between 390°C and 430°C.

8. Nomenclature

C_N = experimental naphthalene concentration ($\mathrm{mol\,g^{-1}}$)
C_{Npyr} = naphthalene concentration due to reaction 2 only ($\mathrm{mol\,g^{-1}}$)
C_N = naphthalene concentration due to reaction 1 only ($\mathrm{mol\,g^{-1}}$)
d = mean dimension of tire granules and particles loaded in the reactor (mm)
f = tire/solution feed ratio ($\mathrm{g\ tire\ g^{-1}}$ solution)
H_D = donated hydrogen at the end of each run ($\mathrm{g\,g^{-1}}$ of tire)
k_{pl} = kinetic constant of reaction 2 ($\mathrm{min^{-1}}$)
p = total pressure in the autoclave (bar)
R = gas constant 8.314×10^{-3} ($\mathrm{kJ\,mol^{-1}\,K^{-1}}$)
T = temperature in the autoclave (°C)
T_b = temperature in the thermogravimetric balance (°C)
t = time (min)
t_S = sampling time (min)
W_t = mass of tire fed to the reactor (g)
W_d = mass of tetralin fed to the reactor (g)
y = molar fraction ($\mathrm{mol\,mol^{-1}}$ hydrocarbons)

9. Glossary

HMWC = high molecular weight compounds ($135 \leq MW \leq 300$) or ($190 < T_b < 320$)
LMWC = low molecular weight compounds ($MW < 118$)
MMWC = medium molecular weight compounds ($118 \leq MW < 135$)
MW   = molecular weight
VHMWC= very high molecular weight compounds ($MW > 300$) or ($T_b > 320$)

Acknowledgements

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