

Hydrogenative pyrolysis of waste tyres: kinetic analysis

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Abstract

A kinetic model for the hydrogenative liquid–solid pyrolysis of waste tyres is presented. The model is tested with available experimental data obtained by running the pyrolysis of tyre particles (size < 500 μm) in a stirred batch reactor, in the presence of tetralin (as hydrogen donor), under a nitrogen atmosphere, and in the temperature range 345–430°C. Because a huge number of products is formed during the pyrolysis process, the compounds have been classified into homogeneous groups. On the basis of the proposed model, a reaction network which describes the evolution of these groups has been set. The kinetic constants of the reactions entering the network have been evaluated at 345, 393, and 430°C. The analytical equations obtained from the model fit the data satisfactorily.

The results of the investigation indicate that the first step of the pyrolysis is the rupture of weak bonds which leads to the dissolution of the tyre particles as large aggregates of molecules, in a time which is of the order of 1 min. Then, much more slowly, lighter products are released from these aggregates. At $T = 430^\circ\text{C}$ the large aggregates are completely transformed into stable compounds, detectable by GC, in about 250 min. At lower temperatures, $T = 345^\circ\text{C}$, after 250 min 40% of the loaded tyre is still present as macromolecules not detectable by GC.

Keywords: Hydrogenative pyrolysis; Waste tyres; Kinetic analysis; Tetralin hydrogen donor; Reaction network

1. Introduction

Studies on the overall conversion and product distribution as a function of the operating conditions for the pyrolysis of waste tyres are available in the literature [1–6]. The results of these investigations are, indeed, very useful for process development

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purposes. The aim of the present paper is to gain an insight into the mechanism of tyre depolymerization reactions and to derive a kinetic model for describing the overall process. This basic aspect of the problem has received minor attention from previous investigators.

We have specifically concentrated our investigation on the liquid–solid pyrolysis process carried out in the presence of a hydrogen donor (tetralin). This process has proved to be very effective in the technology of coal liquefaction. The effect of the presence of tetralin on tyre pyrolysis has been investigated by Liu et al. [1]. However, these authors report essentially on overall tyre conversion and on the yield to oil + gas, as function of the temperature. No information is provided on the chemical products which are formed during the process and on their evolution with reaction time. Therefore a kinetic analysis of the process for obtaining an understanding of the mechanism of tyre depolymerization is not possible with the data of Liu et al. [1].

In a previous paper Murena et al. [6] provide a much more detailed experimental analysis of tyre pyrolysis in the presence of tetralin. Many of the chemicals which are produced both in the liquid and gas phase are identified. Moreover, the evolution of these products, with reaction time, is also provided. In the present paper a kinetic analysis of the process is attempted by identifying the reaction network and by evaluating the kinetic constants of the reactions of the network.

Polymeric materials (coal, rubber, plastics, biomass, etc.) are commonly described as formed of large aggregates of molecules held together by strong covalent bonds. These aggregates are linked together by weaker bonds [7]. Therefore, a two-step mechanism is often proposed for describing the pyrolysis of these materials in a reaction medium. The first step (the quick rupture of the weaker links) leads to the dissolution of the large aggregates which are then depolymerized (second step) much more slowly. The presence of the hydrogen donor plays the role of saturating free radicals, thus avoiding coking reactions.

For the hydrogenative pyrolysis (hydroliquefaction) of coal, a topic which has been much investigated in recent years, the two-step mechanism holds true. In particular, as shown by Gioia and Murena [8,9], the second step may be assumed to take place by a mechanism in which pyrolysis products detach from the aggregates as radicals which are then saturated by the hydrogen donor.

A two-step mechanism can be proposed for hydrogenative tyre pyrolysis also. Information on the characteristic time of the first step is available. In fact, Bouvier and Gelus [2] report a dissolution time of about 70 s for 3-mm-thick samples of sulphur–SBR rubber in oil, at $T = 365^{\circ}\text{C}$. Shorter dissolution times may be predicted at higher temperatures and for smaller particles. Therefore, at the temperatures and for the particle sizes investigated in the present paper, the dissolution time would be around 1 min. The aim of the present paper is to describe the kinetics of the depolymerization of the aggregates (the second step) which is indeed the limiting step of the overall pyrolysis process.

Due to the huge number of compounds produced during pyrolysis [6], the kinetic model must resort to a classification procedure in order to collect the products into a limited number of homogeneous groups. These groups are defined on the basis of analytical and/or practical criteria. The simplest classification criterion collects the

compounds according to the phase in which they are mainly present (gas, liquid, and solid). In more detailed studies investigators classify compounds in standard groups. For example, in coal liquefaction it is common to classify products in the groups: gas; oil (pentane-soluble fraction); asphaltenes (pentane-insoluble but benzene-soluble); preasphaltenes (benzene-insoluble but pyridine-soluble); and solid residue (insoluble in tetrahydrofuran). The method of classification adopted in this paper is based on the procedure described in the previous paper by Murena et al. [6].

2. Experimental procedure and interpretation of data

The apparatus, the experimental method and the analytical technique are described in a previous paper [6] and by Garufi [10].

Steel-free tyre particles from a waste tyre recycling firm were supplied by Eniricerche. In our laboratory the tyre particles were ground by a cryogenic technique, sieved, and the fraction with dimension less than 500 μm was used in pyrolysis runs. Tyre rubber was characterised by thermogravimetric analysis (TGA) following the same procedure as that reported by Williams and Besler [11]. Tyre samples from 3 to 20 mg were loaded on the thermobalance plate and heating rates of 5 and 80 $^{\circ}\text{C min}^{-1}$ were adopted. The rate of weight loss diagram showed the presence of two peaks for both heating rates. When the heating rate was at 5 $^{\circ}\text{C min}$, the first peak was at 370 $^{\circ}\text{C}$ and the second at 450 $^{\circ}\text{C}$. Performing the same analyses with a rubber sample of known composition, containing natural rubber and styrene-butadiene rubber, the same two peaks were detected. These results indicate that the tyre rubber used for pyrolysis runs contains both natural and SBR rubber in about the same proportions. In this paper we indicate the tyre used as 'waste tyre' due to its source.

Pyrolysis runs were carried out in a stirred batch reactor in the presence of pure tetralin (99%; Aldrich) under a nitrogen atmosphere. Tetralin acts as reaction medium and hydrogen donor. The operating conditions are reported in Table 1.

Liquid and gaseous samples were withdrawn at several reaction times. They were analysed by gas chromatography with flame ionization detection. The composition of the liquid samples was directly representative of the concentration versus time pattern due to the pyrolysis reactions in the liquid phase. The same was not exactly true for the gas samples. In fact, after the withdrawal of a gaseous sample the pressure in the reactor dropped by about 5 bar and was immediately restored by introduction of nitrogen. This operation caused a dilution of the pyrolysis products in the gas phase. The dilution effect has been accounted for in order to correctly evaluate the concentration versus time

Table 1
Feed and operating conditions of tyre pyrolysis runs. Run numbers as in Ref. [6]

Run	T ($^{\circ}\text{C}$)	p (bar)	W_{tyre} (g)	d (mm)	W_0 (g)	f (g g^{-1})
5	345	50	6.70	≤ 0.5	99.0	0.067
7	393	50	6.82	≤ 0.5	91.0	0.075
8	430	50	4.92	≤ 0.5	91.8	0.054

pattern due to reactions producing gaseous compounds. Moreover, the compounds produced by the parallel reactions of tetralin pyrolysis were identified by blank runs carried out by loading pure tetralin in the reactor. These compounds were not considered in the analysis of the tyre pyrolysis network.

A thermogravimetric (TG) balance was also used to analyse liquid samples at the beginning and at the end of the pyrolysis runs. As the final result of the analytical procedure we obtained for each run:

- the concentrations of pyrolysis products, as a function of the reaction time, in both gas and liquid phases, by GC analysis,
- the residual weight versus the balance temperature for the liquid samples withdrawn at the beginning and at the end of each run, by TG analysis.

2.1. Classification procedure

About 150 reaction products were detected by GC in both the liquid and the gas phase [6]. Therefore the development of the kinetic analysis needs a simplifying procedure. In the previous paper [6] a classification procedure was already set and four homogeneous groups were defined in the liquid phase and twelve groups in the gas phase. In this paper the classification procedure is somewhat refined in order to further reduce the number of groups on which to base the kinetic analysis.

Two different properties were utilized in order to classify the compounds present in the liquid samples. These properties were defined according to the analytical procedure adopted. In particular, compounds identified by GC were grouped according to their elution time. Compounds detected by TG were grouped according to the temperature at which they were vaporized.

The groups defined in the liquid phase are:

- **LL** (light liquid compounds); evaluated by GC, which includes pyrolysis products eluted before tetralin and naphthalene (products with $MW < 135$).
- **HL** (heavy liquid compounds); evaluated by GC, which includes pyrolysis products eluted after tetralin and naphthalene ($MW > 135$). It must be pointed out that the efficiency of GC analysis for this group is controlled by the injector temperature which was set at $T = 320^\circ\text{C}$. Calibration runs had shown that compounds with $MW > 300$ were not detected. Moreover, analysis with standard compounds showed that the response factor (area%/wt%) is ≈ 1 for compounds with $MW \leq 230$ and decreases to 0.2 for compounds with $MW \leq 300$. Due to the high number of pyrolysis products detected in the liquid phase a response factor = 1 was assumed for all analysis. For this reason the analysis of HL group by GC can underestimate the actual concentration of this group, depending upon the median molecular weight of the group. The concentration of the HL group was also evaluated by TG in the samples collected at the beginning and at the end of each run. In this case the amount of HL group is evaluated as the residual weight on the balance at $190^\circ\text{C} \leq T \leq 320^\circ\text{C}$. The lower limit is the temperature at which the complete evaporation of tetralin and naphthalene takes place as evaluated by a blank run [6]. The upper limit is set equal to the temperature of the GC injector.
- **VHL** (very heavy liquid compounds); evaluated by TG, includes pyrolysis products

which were not detected by GC. The amount of this group was evaluated as the residual weight on the balance at $T \geq 320^\circ\text{C}$.

The groups in the gas phase were defined on the basis of the number of carbon atoms and of the presence of unsaturated C–C bonds:

- **LG** (light gases); compounds with 1–3 carbon atoms.
- **UG** (unsaturated gases), unsaturated compounds with more than three carbon atoms.
- **SG** (saturated gases); saturated compounds with more than three carbon atoms.

Because the GC analyses were carried out for all (liquid and gaseous) samples withdrawn during the reaction run, concentrations as a function of the reaction time are available for the groups LG, UG, SG, LL and HL. However, the concentration of the VHL group is available only at the time of the first and last sampling. The same holds true for the concentration of HL by TG.

An alternative to the above reported classification criterion was to group together the compounds belonging to the same classes (e.g.; paraffins, olefins, aromatics, polycyclic aromatics). We have preferred to adopt the above reported classification criterion which is more convenient for the subsequent kinetic analysis.

In Figs. 1–3 (a figure for each reaction temperature) the experimental concentration data versus reaction time for the above groups are reported. All concentrations are expressed as g g^{-1} of loaded tyre.

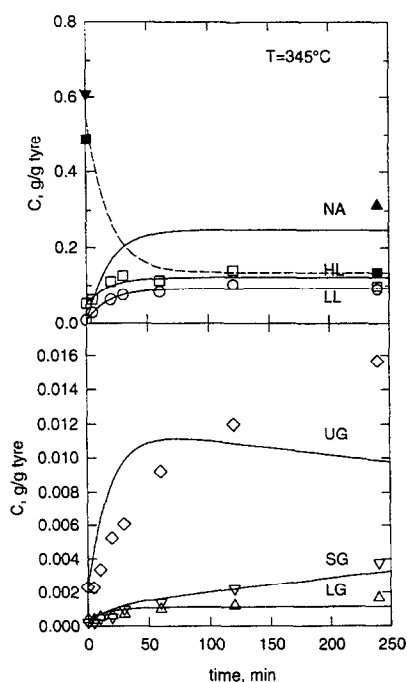


Fig. 1. Concentration of tyre pyrolysis products versus reaction time for run 5. Operating conditions are given in Table 1. Symbols are: LL (\circ); HL (\square); LG (\triangle); SG (∇); UG (\diamond); VHL (\blacksquare); HL by TG (\blacktriangle), T_{pyr} (\blacktriangledown). Fitting curves are based on the network of Figs. 1 and 4 and kinetic constants of Table 2.

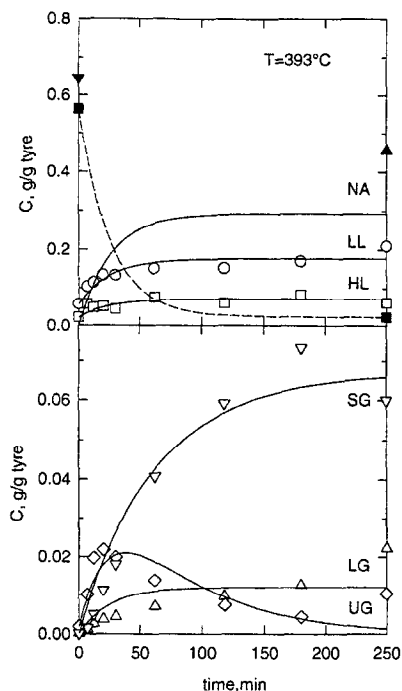


Fig. 2. Concentration of tyre pyrolysis products versus reaction time for run 7. Operating conditions are given in Table 1. Symbols are: LL (○); HL (□); LG (△); SG (▽); UG (◇); VHL (■); HL by TG (▲); T_{pyr} (▼). Fitting curves are based on the network of Figs. 2 and 4 and kinetic constants of Table 2.

In each figure the data reported are as follows:

- experimental concentration of light liquid (LL), heavy liquid (HL), light gas (LG), unsaturated gas (UG) and saturated gas (SG) at each sampling time. These data points are indicated by empty symbols (see captions);
- experimental concentration of very heavy liquid compounds (VHL) as measured by TG at the beginning and at the end of each run. These data points are reported as full squares;
- the fraction of the tyre which can undergo pyrolysis (T_{pyr}), obtained by subtracting from unity the fraction of the loaded tyre which was collected at the end of each run as solid residue insoluble in tetrahydrofuran [6]:

$$C_{T_{pyr}} = 1 - \frac{W_{SR}}{W_{tyre}} \quad (1)$$

where W_{SR} and W_{tyre} are, respectively, the amount of solid residue collected at the end of each run and the amount of loaded tyre. The value of $C_{T_{pyr}}$ is reported in Figs. 1–3 with a reverse full triangle at $t = 0$;

- experimental concentration of heavy liquid compounds (HL) as measured by TG at the end of each run, as full triangles;

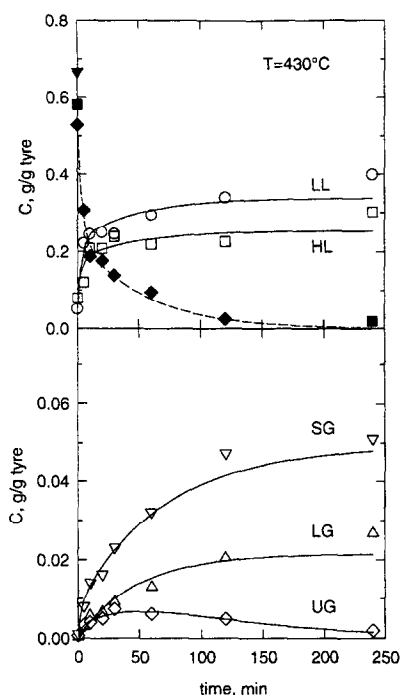


Fig. 3. Concentration of tyre pyrolysis products versus reaction time for run 8. Operating conditions are given in Table 1. Symbols are: LL (○); HL (□); LG (△); SG (▽); UG (◇); VHL (■); HL by TG (▲), T_{pyr} (▼). Fitting curves are based on the network of Fig. 4 and kinetic constants of Table 2. Full diamonds symbols adopted for VHL as calculated by the mass balance (see Eq. (8))

- continuous curves which represent the model predictions to be discussed below. The meaning of the continuous curves labelled NA will be discussed later.

The runs on which our analysis is based are those carried out at the temperatures: 345, 393 and 430°C. They cover the temperature range of practical interest.

3. Depolymerization mechanism and reaction network

Inspection of Figs. 1–3 shows that at the time of the first sampling ($t \cong 1$ min) the reaction products are mainly compounds belonging to VHL group and in smaller amounts gas and lighter liquid compounds. At this time the sum of the concentrations of all the products detected, both in the liquid and in the gas phase (VHL, LG, UG, SG, LL and HL), matches the amount of the fraction of the tyre that can undergo pyrolysis $C_{T_{\text{pyr}}}$. This indicates that dissolution of the tyre in the liquid is complete in about 1 min, which is in accordance with the dissolution time measured by Bouvier and Gelus [2].

As the pyrolysis proceeds the VHL compounds react further forming lighter products, both gaseous and liquid. Examining the concentrations of VHL (Figs. 1–3) it appears

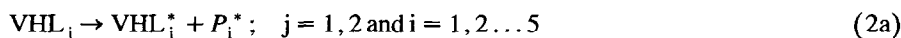
that at $T = 430^\circ\text{C}$ almost complete conversion of the tyre is achieved at the end of the run ($t = 240$ min). In contrast, at $T = 345^\circ\text{C}$ ($t = 240$ min) about 13% of the loaded tyre is still present as VHL compounds.

These experimental observations indicate that tyre hydrogenative pyrolysis is a two-step process. The first step is the quick dissolution of the tyre in the reacting mixture as VHL compounds. They have been detected by TG as the residual weight on the balance at $T \geq 320^\circ\text{C}$. Lacking a precise identification of VHL compounds they can be described as large aggregates of molecules dissolved in the liquid phase. Only small amounts of gaseous and lighter liquid compounds are formed during this step. During the second step, on a much longer time scale, VHL compounds pyrolyse to lighter compounds (LL, HL, LG, UG and SG). In the second step the hydrogen donor is considered to play the role of saturating free radicals and avoiding coking reactions. Thus, the kinetic analysis will be focused on the second step of the whole process since the first step takes place on a time scale much smaller than that explored in this work.

Further inspection of Figs. 1–3, shows that the concentration versus time data for all products have a finite derivative at $t = 0$, thus indicating that all pyrolysis products, independently of their molecular weights, are simultaneously produced from the beginning of the process. The above consideration lets us assume that the hydrogenative pyrolysis of tyres takes place essentially through a parallel reaction network.

The experimental data reported in Fig. 3 show that in the first 50 min, there is a rapid growth of product concentration followed by a slower one. A similar but less clear pattern is observed also in the other runs (Figs. 1 and 2). This pattern can be explained if we describe the complex structure of VHL as formed of two parts of different reactivity. The reactivity of the first part is larger than that of the second part which, presumably, is the SBR fraction of the tyre. At the end of the run at $T = 430^\circ\text{C}$ the VHL group results indicate that it has completely reacted and its concentration approaches zero. This is an indication that at this temperature both fractions of VHL compounds react. Lowering the temperature, the concentration of VHL group at the end of the run does not reach a zero value. This is an indication that, at these temperatures, a fraction of VHL does not react during the observed reaction time.

Assuming that the pyrolysis products have a molecular weight much smaller than the median molecular weight of VHL group, the process can be described by a cyclic mechanism: any reaction of the cycle determines the detachment of a lighter molecule from a compound belonging to the VHL group. This mechanism is analogous with the depolymerization mechanism already proposed for coal liquefaction [9]. The role of tetralin in the process is the donation of the hydrogen atoms necessary to saturate the free electrons. The pyrolysis reactions of VHL should be written for each reaction product. However, having combined these products into a few groups, only a limited number of reactions need to be considered. The reactions which describe the pyrolysis of VHL group are:



where:

VHL_j = one of the two fractions of the VHL group, namely VHL₁ or VHL₂;

T = tetralin;

P_i = one of the homogeneous groups of products previously defined: LG, UG, SG, LL or HL;

N = naphthalene produced by tetralin dehydrogenation;

α, α' and β = stoichiometric coefficients;

VHL_j^{*} and P_i^{*} = free radicals.

Index j indicates the fractions into which the VHL group is subdivided and index i indicates the different groups of pyrolysis products. Assuming first-order kinetics for each reactant the rate of formation of the radical P_i^{*} is given by:

$$\frac{dC'_{P_i^*}}{dt} = k'_{ji} C'_{VHL_j} - k'_i C'_{P_i^*} C'_T \quad (3)$$

where k'_{ji} is the kinetic constant of reaction 2a and k'_i is that of reaction 2b. The right-most term in Eq. (3) is the rate of reaction 2b which also gives the rate of formation of the group P_i:

$$\frac{dC'_{P_i}}{dt} = k'_i C'_{P_i^*} C'_T \quad (4)$$

Assuming that in this process the slow step is reaction 2a (i.e. reaction 2b is so fast as not to matter), a steady-state approximation for radicals is the usual assumption and gives:

$$\frac{dC'_{P_i}}{dt} = k'_{ji} C'_{VHL_j} \quad (5)$$

Concentrations C' in Eqs. (3)–(5) are expressed in moles per volume of liquid phase. Since we are interested in the conversion of tyre into liquid and gaseous products, it is more significant if the concentrations are expressed in grams per gram of loaded tyre. In this case Eq. (5) becomes:

$$\frac{dC_{P_i}}{dt} = k_{ji} C_{VHL_j} \quad (6)$$

where C_{P_i} and C_{VHL_j} are in grams per gram of loaded tyre. It must be observed that the loaded tyre is a steel-free tyre. Therefore concentrations are grams per gram of steel-free tyre. k_{ji} in Eq. (6) is the first-order kinetic constant of the reaction of production of group P_i from the fraction j of the VHL group. Comparing Eq. (6) with Eq. (5) gives:

$$k_{ij} = k'_{ij} \frac{MW_{P_i}}{MW_{VHL_j}} \quad (7)$$

where MW_{P_i} and MW_{VHL_j} are the median molecular weights of the group P_i and of the dissolved tyre fraction VHL_j. Since experimental concentrations evaluated by GC and TG are in terms of grams per gram of solution, they are simply transformed into terms

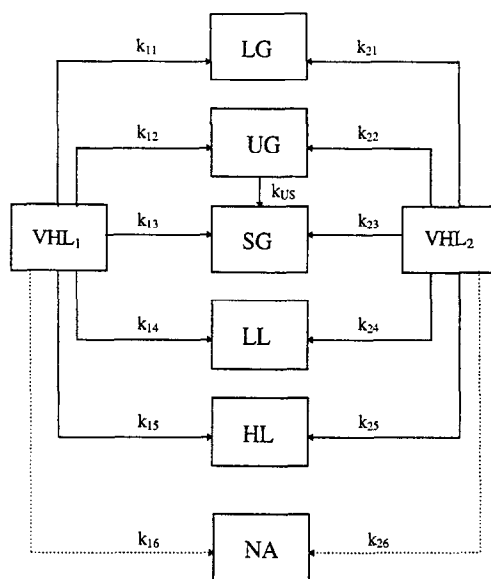


Fig. 4. Tyre pyrolysis reaction network in the presence of a hydrogen donor (tetralin). Dashed lines are for runs at 345 and 393°C.

of grams per gram of loaded tyre. Then, using Eq. (6), median molecular weights of P_i groups and of VHL_j fractions are not necessary to evaluate k_{ji} values.

In writing the reaction network several alternatives are possible. The procedure we have adopted for evaluating them is based on trial and error. We have, firstly, considered different chemically possible reaction networks. For each possible network the kinetic constants are estimated by a statistical method discussed later. All the networks which produce inconsistent kinetic constants are discarded. Although many possibilities are excluded, a few alternatives still remain. For the remaining networks the theoretical curves are compared with the experimental C versus t data.

The reaction network which best describes the hydrogenative pyrolysis of tyres during the second step is that reported in Fig. 4. In the network of Fig. 4 the NA group not previously defined is reported. NA stands for: 'Not quantitatively Analysed HL Compounds'. We had to introduce this group because the mass balance at $t = t_f$ does not check for the runs at $T = 345$ and $T = 393^\circ\text{C}$. We assume that the deficiency in the mass balance (at 345 and 393°C) is due to the underestimation of the HL group by GC, as reported in the 'Experimental procedure' section.

At the end of the runs carried out at 345 and 393°C compounds belonging to the VHL group are still present. Therefore after 250 min the pyrolytic process is not complete. Furthermore, by comparing the amount of HL measured by GC (empty square at $t = t_f$) with that measured by TG (full triangle) it can be observed that the concentration of HL measured by TG at the end of these two runs is larger than HL by GC. The amount of HL by TG correlates very well with the sum of NA and HL as measured by GC. Conversely, at $T = 430^\circ\text{C}$ (see Fig. 3) both parts VHL_1 and VHL_2 are degraded to gas

and light liquid compounds (VHL at t_f is $\cong 0$) and the mass balance is well checked at the end of the reaction run. We must assume that the HL group is, in this case, quantitatively detected by the GC, i.e. the median molecular weight of this group of compounds is low ($135 < MW < 230$). As a consequence, for the run carried out at $T = 430^\circ\text{C}$, the introduction of the NA group in the network of Fig. 4 is not necessary.

The procedure adopted for evaluating the kinetic constants of the network in Fig. 4 for the run at $T = 430^\circ\text{C}$ is as follows. The concentration of the VHL group is calculated in correspondence with each sampling time by the mass balance equation:

$$C_{\text{VHL}} = C_{T_{\text{pyr}}} - \sum_{i=1}^5 C_{\text{P}_i} \quad (8)$$

where C_{VHL} stands for the concentration of VHL group (i.e. $C_{\text{VHL}} = C_{\text{VHL}_1} + C_{\text{VHL}_2}$), $C_{T_{\text{pyr}}}$ for the concentration of the tyre fraction which can undergo pyrolysis (see Eq. (1)), and $\sum_{i=1}^5 C_{\text{P}_i}$ is the sum of the concentrations of the pyrolysis products detected by GC: LG, UG, SG, LL and HL.

The VHL concentration, as calculated by Eq. (8), is reported in Fig. 3 with full diamonds. These calculated concentrations were used to evaluate the first-order kinetic constants of the two reactions: $\text{VHL}_1 \rightarrow \text{products}$ and $\text{VHL}_2 \rightarrow \text{products}$ according to the kinetic equations:

$$\frac{dC_{\text{VHL}_j}}{dt} = -k_{\text{VHL}_j} C_{\text{VHL}_j} \quad (9)$$

where:

$$k_{\text{VHL}_j} = \sum_{i=1}^5 k_{ji} \quad (10)$$

From Eq. (10), k_{VHL_1} and k_{VHL_2} are the overall kinetic constants for the pyrolysis of the two fractions into which we have schematically divided the dissolved tyre, i.e. VHL_1 and VHL_2 . Initial values $C_{\text{VHL}_1}^0$ and $C_{\text{VHL}_2}^0$ must be known to solve Eq. (9). A best-fitting procedure was used to calculate at the same time the kinetic constants of Eq. (9) and the initial values of $C_{\text{VHL}_1}^0$ and $C_{\text{VHL}_2}^0$. It was found that $C_{\text{VHL}_1}^0 = 0.36$ (g g^{-1} loaded tyre) and $C_{\text{VHL}_2}^0 = 0.30$ (g g^{-1} loaded tyre). Therefore the two fractions represent 54 wt% and 46 wt% of the fraction of the tyre which can undergo pyrolysis (T_{pyr}). The concentrations of VHL_1 and VHL_2 are then evaluated at each sampling time by solving Eq. (9). The set of differential equations describing the network in Fig. 4 are then written assuming first-order kinetics (see Eq. (6)). The method proposed by Himmelblau et al. [12] is used to evaluate the kinetic constants of the network in Fig. 4.

It must be noted that at 430°C , with both parts VHL_1 and VHL_2 having measurable reactivities, it was possible to evaluate all the kinetic constants entering the reaction network of Fig. 4. In contrast, at 345 and 393°C the statistical analysis of the data points did not permit statistically significant evaluation of the kinetic constants of the reactions which led from VHL_2 to lighter compounds (i.e. k_{2i} are much smaller than k_{1i}). For these two runs a simplified network was adopted in which only reactions $\text{VHL}_1 \rightarrow \text{P}_i$

Table 2
Kinetic constants (k_{ij} [$=$] min^{-1}) of the reaction network in Fig. 4

T ($^{\circ}\text{C}$)	Reactant	k_{11}	k_{12}	k_{13}	k_{14}	k_{15}	k_{16}	k_{US}
		k_{21}	k_{22}	k_{23}	k_{24}	k_{25}	k_{26}	
345	VHL ₁	$9.56 \cdot 10^{-5}$	$1.23 \cdot 10^{-3}$	$1.35 \cdot 10^{-4}$	$1.08 \cdot 10^{-2}$	$9.01 \cdot 10^{-3}$	$3.19 \cdot 10^{-2}$	$7.99 \cdot 10^{-4}$
	VHL ₂	–	–	–	–	–	–	
393	VHL ₁	$8.36 \cdot 10^{-4}$	$2.54 \cdot 10^{-3}$	$2.05 \cdot 10^{-3}$	$8.42 \cdot 10^{-3}$	$3.51 \cdot 10^{-3}$	$2.07 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$
	VHL ₂	–	–	–	–	–	–	
430	VHL ₁	–	$2.0 \cdot 10^{-3}$	$7.0 \cdot 10^{-3}$	$1.7 \cdot 10^{-1}$	$9.9 \cdot 10^{-2}$	–	$1.2 \cdot 10^{-2}$
	VHL ₂	$1.8 \cdot 10^{-3}$	$9.2 \cdot 10^{-4}$	$2.3 \cdot 10^{-3}$	$9.3 \cdot 10^{-3}$	$6.0 \cdot 10^{-3}$	–	

and reaction $\text{UG} \rightarrow \text{SG}$ were considered. To perform the statistical analysis for the runs at $T = 345$ and 393°C we assumed that at these temperatures the fraction VHL_2 does not react and that the VHL concentration still present at $t = t_f$, as measured by TG, represents the fraction VHL_2 of the tyre, the remaining part being VHL_1 . As a consequence at any time $C_{\text{VHL}} = \text{VHL}^{\text{if}}$, which is constant with reaction time, and $C_{\text{VHL}_1} = C_{\text{VHL}} - \text{VHL}^{\text{if}}$. VHL^{if} stands for the concentration of VHL as measured by TG at the end of each run (see Figs. 1–3 full square symbol). By a best fitting procedure, similar to that adopted for the run at $T = 430^{\circ}\text{C}$, the kinetic constants of the left-hand side of the network in Fig. 4 have been evaluated.

The values of the kinetic constants of the network in Fig. 4 are reported in Table 2 and the corresponding fitting curves in Figs. 1–3. As regards the use of the kinetic constants reported in Table 2, it must be recalled that: the tyre is a steel-free tyre, the concentrations must be expressed in terms of grams per gram of loaded tyre, and all the reactions are assumed to take place mainly in the liquid phase where a large amount of the hydrogen donor (tetralin) is present. However, for the reaction $\text{UG} \rightarrow \text{SG}$ the reactant is present mainly in the gas phase. Therefore, assuming that physical equilibrium exists between the two phases, the values of the corresponding kinetic constant k_{US} reported in Table 2 include the Henry's constant and depend on the size of the reactor adopted.

Inspection of Fig. 3 shows that at $T = 430^{\circ}\text{C}$ fitting is satisfactory and the kinetic model describes the different patterns of the experimental data points. In particular, introducing the two parts of the VHL compounds; i.e., VHL_1 and VHL_2 , the model is able to follow the initial high rate of production of pyrolysis products (see curves reported in Fig. 3) due to the high reactivity of VHL_1 , and the successive slow rate of reaction of VHL_2 .

Inspection of Fig. 2 shows that at $T = 393^{\circ}\text{C}$ the fit is still satisfactory even though the simplified network, which excludes the reactions of VHL_2 , has been used. The same holds true for the run at $T = 345^{\circ}\text{C}$ (see Fig. 1). However, in this case the fitting of the gas phase data (bottom part of the figure) is less accurate. This is due to the exceedingly low amounts of gases formed at this temperature (less than 0.02 g g^{-1} loaded tyre).

The theoretical pattern of concentration of the reactant VHL, reported as dashed lines in Figs. 1–3, can be compared with the experimental data of the VHL group, available at the beginning and the end of each run (Figs. 1–3). We observe that at all temperatures

experimental values VHL^0 and VHL^{tf} are very close to the corresponding values predicted by model curves. This confirms the hypothesis that the VHL group is the reactant of the hydrogenative pyrolysis process. At $T = 345^\circ\text{C}$ the value C_{VHL}^0 predicted by the model curve is greater than the experimental value VHL^0 as measured by TG. This can be explained by considering that at this temperature the rate of dissolution of the tyre particles is slower (i.e. the first step takes a longer time), hence at the moment of the first sampling the dissolution step is not yet complete. In this case the difference $C_{VHL}^0 - VHL^0$ is the amount of that part of pyrolysable tyre (T_{pyr}) whose dissolution did not take place before the first sampling.

4. Conclusions

The kinetics of the pyrolysis of tyre in the presence of a hydrogen donor (i.e., tetralin) has been investigated at temperatures of 345, 393 and 430°C . A huge number of pyrolysis products is formed during the process. In order to perform kinetic analysis of the experimental data, it was useful to classify these products in six homogeneous groups (three in the liquid phase and three in the gas phase).

The analysis has shown that tyre pyrolysis process takes place in two steps. The first step leads to the quick dissolution into the reaction medium of the fraction of tyre which can undergo pyrolysis, mainly in the form of compounds having a very high molecular weight. The presence of these compounds has been proved by TG analyses. This first step takes place on a time scale of the order of one minute, which is much smaller than that explored in this work. Therefore, no detailed information is provided for the kinetics of this step.

After the dissolution step the pyrolysis process takes place much more slowly, producing lighter compounds in both the liquid and the gas phase.

The kinetics of the second step has been studied in detail. The reaction network which best fits the experimental data has been identified. The network suggests that pyrolysis products are formed by parallel reactions from the very high molecular weight compounds produced during the first step. The analysis of the experimental data let us conclude that these very high molecular weight compounds comprise two fractions with different reactivities, the less reactive fraction is presumably richer in more complex aromatic compounds. At $T = 430^\circ\text{C}$, in about 250 min, both fractions are completely transformed into stable compounds detectable by GC. At lower temperatures, $T = 345^\circ\text{C}$, after 250 min 40% of the loaded tyre is still present as macromolecules not detectable by GC. The kinetic constants of reactions involved in the network have been evaluated in the temperature range investigated.

5. Nomenclature

$C_{T_{pyr}}$ = concentration of the fraction of the tyre which can undergo pyrolysis (see Eq. (1)); (g g^{-1} of tyre).

C' = concentration; (mol L^{-1} solution)

C = concentration; (g g^{-1} loaded tyre)

f = feed ratio; (g tyre g⁻¹ solution)

k_{ji} = kinetic constant of the reaction $VHL_j \rightarrow P_i$; (min⁻¹)

P_i = homogeneous group of pyrolysis products ($P_i \equiv LG, UG, SG, LL$ or HL)

t_f = final time of tyre pyrolysis runs; (min)

T_{pyr} = fraction of tyre which can undergo pyrolysis (see Eq. (1)).

VHL^0 = concentration of VHL as measured by TG at $t = 0$; (g g⁻¹ loaded tyre)

VHL_1 = more reactive fraction of VHL

VHL_2 = less reactive fraction of VHL

VHL^{t_f} = concentration of VHL as measured by TG at $t = t_f$; (g g⁻¹ loaded tyre)

W_d = mass of tetralin fed to the reactor; (g)

W_{tyre} = mass of tyre fed to the reactor; (g)

5.1. Subscripts

i = index of groups of products identified by GC (LG = 1, UG = 2; SG = 3; LL = 4; HL = 5)

j = index of the VHL fractions: $j = 1$ or 2

5.2. Superscripts

0 = at time $t = 0$

t_f = at the end of the run

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