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PYROLYSIS OF RUBBER AND TYRES WASTE

par

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ABSTRACT

On the request of the European Economic Community the present study has been carried out by the Bureau de Recherches Géologiques et Minières and the Université Technologique de Compiègne.

It gathers the scientific and technical data about the pyrolysis of rubber and tyres waste with a particular emphasis on raw material recovery.

Nowadays, only the solid residue may be recycled as secondary charcoal : gas and liquid may be reused only as source of energy.

Four processes seem interesting for futur developments : Tyrolysis Process, DRP Hambourg University Process, Technology University of Compiegne, IFP Process, Kutrieb Process. Some recommendations can be given : optimize the recycling of existing processes products, study an intermediary way of recuperation of rubber waste, at middle distance between pyrolysis and regeneration.

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GENERAL INTRODUCTION

In 1976 and 1977 the European Economic Community has asked the Bureau de Recherches Geologiques et Minières (B.R.G.M.) assisted by the Kunststoffen en rubber instituut (T.N.O), to gather technical and economical data about rubber and tyres waste recovery in the E.E.C. countries - (BRGM report 77 SGN 547 MIN).

Today, it has appeared necessary to establish the state of the art of a way of development which was full of promise in this time, the pyrolysis.

The present study has been realized ty the B.R.G.M. in collaboration with the Université Technologique de Compiègne. The aim of the work is to gather the scientific and technical data about the principes, processes and results of the pyrolysis applied to the treatment of rubber and tyres waste with a particular emphasis on raw materials recovery.

The enquiry has been operated by writing, visiting, and bibliographical means. As a matter of fact, numerous letters have had no reply or negative answers because of the surrender of several projects.

Only four processes, today, may present an industrial interest. They will be detailed after presentation of the scientific basis and potential efficiency of the pyrolysis of rubber and tyres waste .

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I. PYROLYSIS OF RUBBER AND TYRES : SCIENTIFIC APPROACH

1. INTRODUCTION.

The pyrolysis of organic high grade waste has appeared like a more and more attractive way to solve the problems of proliferation of these waste, especially during 1970-75 years. Pyrolysis is the transformation of chemical compounds by heat without the intervention of secondary reagents, (like oxygen). The chemical reactions are complex and transforme the waste into three fractions : gas, liquid and solid.

In the case of rubber and tyres, the pyrolysis seems to be the main to recover some raw materials the recycling of which, if their properties allows it, could improve the beneficiation of these waste. But such an operation of good and constant quality materials from pyrolysate can be carried out only by using sophisticated and expensive technics : from the laboratory tests about the cinetic of degradation by thermogravimetric analysis or by flash-pyrolysis of the organic product until the full scale unity of treatment, the way is long with many obstacles and a lot of technical and economical realities moderate hopes and solicit new ideas. Nowadays, some processes are in development and already giving some interesting elements for the chemical beneficiation.

So it is necessary, in a first time, to present the scientific data concerning :

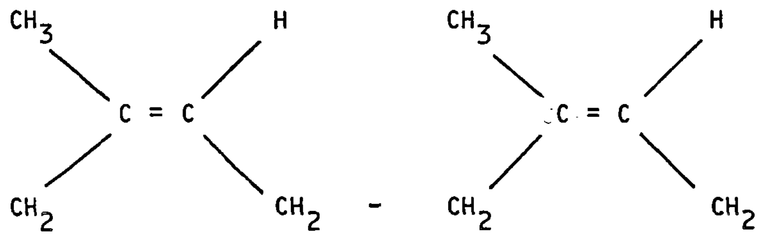
- the nature of the vulcanizated rubbers,
- the cinetic of the pyrolysis of rubber,
- the physical-chemical properties of products of their thermic degradation.

2. GENERALITIES : COMPOSITION AND STRUCTURE OF RUBBERS.

The use of natural or synthetic elastomers is very common in all the types of activities which need of a principal propertie : the high elasticity. The linear and very long macromolecules are elastic if their structure allows the moving of atoms by supplying with of energy, the quantity depending on the nature of macromolecular chain's components.

The main component of rubbers and tyres is the natural or synthetic gum (table 1).

The natural rubber includes macromolecular chains the monomer of which is the methyl -2 butadiene -1,3 or isoprene, generally in 1,4 cis position :



polyisoprene -1,4 cis

Components	New tyre weight %	Used tyre weight %
gum	37	35
carbon black	22	21
extender oil	11	10,5
adjuvants (sulphur)	3,7	3,5
steel rod	13	15
steel net	3	4
textile	10,3	11

TABLE n° 1 - Average composition of a car radial tyre (average weight : 6,8 kg).

The average molecular weight is between 200 000 and 400 000. Because of its particular properties, the natural rubber concerns a lot of applications : in the field of tyres, its is found mainly in the products heavy lorries, agricultural and public works engines. For economic reasons and regulation of supplying, synthetic rubber has served as substitue for natural products since the second world war.

Synthetic rubbers are obtained by radicalar polyaddition of monomers :

. vinylic monomers are used in the production of saturated elastomers (EPDM by example),

. dienes in the production of unsatureted elastomers (pylobutadiene, polyisoprene, by example).

Emulsion is the more utilized process of vulcanization. The styrene-butadiene capolymer, obtained by synthesis, is the main component of car tyres. Elastomer cannot be used alone because its plasticity is too high. The strengths of molecular interaction are weak : if the sample is subjected to a traction, chains may clip one an another and the deformation is irreversible. That is why it is necessary to increase the intermolecular linkages without cramping the deformations of chains. It is the job of the vulcanization which products a selected and limited number of covalent chemical linkages between the macromolecules.

The more employed processes of vulcanization use sulphur or peroxydes. The sulphur vulcanization is the more common way of crosslinking because it is applicable to all elastomers bearing double-linkages.

To increase the cinetic of the reaction producing carbon-sulphur linkages, catalysts (or accelerators) and other adjuvants must be added.

The peroxide-vulcanization is applicable to all the hydrocarbonated chains but needs of presence of enough moving atoms of hydrogen. In a first step, there is decomposition of peroxide, and after fixation of root, or by elemination of an atom of hydrogen, or by fixing on a an unsaturated carbon (allylic by example). The cross linking is realized by carbon-carbon linkages. These technics are less common than sulphur vulcanization but need no other reactive.

In conclusion, vulcanization produces, from a linear polymer, a three dimensional entanglement.

The mechanical properties of vulcanizated rubbers are influenced by the adding, before vulcanization, of loading products which are inert, like talc, or strengthenning like carbon black.

During the fabrication, others products are added like antioxydizings the goal of which is to prevent the ageing of the rubber. Because of the generalization of radial frame tyres, the quantity of stell is not negligeable (see table 1).

The wear and tear of a tyre putdown near to 10 % of the weigh ot the tread of a tyre.

These outlines show the diversity of rubbers, depending of :

- choice of one or some main macromolecules,
- the nature of adjuvants and loads,
- the type of vulcanization.

That foreshadows the complexity of mixtures resulting of the pyrolysis of rubber wastes especially in liquid and solid phases.

There are two big classes of rubber objects :

- tyres, which are composite because the required properties of tread and sides are very different (their production represents near to 65 % of the elastomer consumption) ;

- industrial rubbers which are very varying (tubs, belts, packings, coatings...).This heterogeneity is found again in the waste which, contrary to old tyres, are very scattered and more difficult to collect.

Because of the more important concentration of tyres, research workers and manufacturers have favoured the treatment of tyres and subsequently adjust the technics of pyrolysis. Because of the difficulties of collect and the lowness of the individual stocks, other rubber waste have been neglected.

So, the main data here presented, are concerning the pyrolysis of tyres or rubber works presenting similar composition and properties.

3. THE POTENTIAL ADVANTAGES OF THE PYROLYSIS.

Rubber and tyres have not only a high heating value but also a high heating content including the manufacture and raw materials production energy. So, it is important to analyse the recycling of waste in term of presentation of the energetic content.

From the data of W.L. COX (1) concerning the energetic content of the main components of rubbers (table 2), it can be seen that nowadays, the rubber industry is more subordinate to fossil energy, especially petroleum. So, from 1950 until 1970, the energetic content of rubber has increased until 50 % because of the growing use of synthetic rubber and carbon black.

Raw material	Energetic content, Kcal/kg
Natural rubber	0
Synthetic rubber (SBR)	13 300
Carbon black	22 200
Extender oil	10 000
New tyre	19 400

TABLE 2 - Energetic content of raws materials of rubbers and tyres (1).

The energetic content of a tyre is estimated at 19 400 Kcal/kg and the goal of its recycling is to recover the maximum of this energy. From the preliminary tests of the American Bureau of Mines (2), the pyrolysis at 500° C of one kilogram of car tyre waste produces 0.4 kg of carbon black, i.e. an equivalent of 8 880 Kcal, 0.49 kg of oil, i.e. 4 900 Kcal and 0.05 kg of gas i.e. the equivalent energy need for the running of the pyrolysis. By this way it is possible to recover 13 780 Kcal/kg ; i.e. an efficiency of 71 %. This simple appreach explains the interest raised up by the pyrolysis at the beginning of years 70 because it appeared the better mean to conserve the energetic content. During the same time regeneration and retreading, well known in term of energetic content conservation, were regressing because of technical and economical·reasons.

4. HIGH TEMPERATURE BEHAVIOUR OF RUBBERS.

It will be dealt with the behaviour of rubbers at more than 300° C temperatures in inert atmosphere elastomers from natural rubber and styrene-butadiene copolymer (S.B.R.) i.e. raw materials of tyres, will be especially investigated.

4.1. Thermal stability of natural rubber and S.B.R.

Thermogravimetric analysis is a good method to study the thermal stability of elastomers and the cinetic of the phenomena of thermal degradation. Scientists and technicians use it frequently and mainly to study the influency of the elastomer structure and the conditions of formulating, to identify the nature of elastomers and adjuvants in a given vulcanizate (monitoring tests). So most authors have observed that the thermal degradation of elastomers under nitrogen atmorphsere is exothermic with an exotherm centred near to 380° C. They specify that the exothermocity proceeds likely from cycle formation and crosslinking and the whole reaction can be classed as a first order reaction, the activation energy of which is 32 to 35 kcal/mole. This exothermic reaction comes before the polymer decomposition. S.L. NADORSKY (3) gives some data on the vacuum pyrolysis of a commercial styrene (25 %) butadiene (75 %)

copolymer after cleaning by dissolution in the benzene and precipitation by the methanol (table 3). A light fraction F1 is obtained in small quantity (C1 to C6) and middle fraction F2 includes waxes (M1 = 712). There production of styrene but presence of butadiene 1,3 which however represents only an average of 2 % of the pyrolysis products. Moreover, like it can be seen in figure 1, the comparaison between the natural rubber and the styrene-butadiene copolymer shows the better stability of the S.B.R. (4).

Pyrolysis temperature, ° C	styrene-butadiene copolymer		
	pyrolysed material %	F1 %	F2 %
325	6.9	11.6	88.4
375	5.6	12.6	87.4
400	71.7	8.7	91.1
425	94.6	7.6	92.4

TABLE 3 - Loss of weight versus pyrolysis temperature.

Some authors have taken advantage of these thermograms to determine the cinetic parameters of the decomposition reaction, especially its order and activation energy. So, D.A. SMITH (5), working in non-isotherm conditions, has shown that the order of the reaction is 1, determined the cinetic constant kp at different temperatures and deduced the value of the activation energy. Moreover, in the case of S.B.R. (figure 2), he has proved the presence of two competitive first order reactions, activation energy of which are 9 Kcal mole^{-1} and 55 Kcal mole^{-1} D.A. SMITH precises that these results are according with anterior data obtained in isotherm conditions and depending of the size of the sample and the vulcanization. FLYNN and WALL (6) consider that the first order of the reaction is at one and the same time global and empirical.

A lot of works on the beheviour of rubbers in the field of temperature where they decompose have been realized from 1950 to 1970 but their goal was not the settlement of parameters necessary to the feasibility of a pyrolysis operation. It is only known that the vulcanized or not vulcanized elastomers decompose between 380° and 500° C. But the pyrolysis cinetic, the nature of limiting parameters and behaviours of formulated rubbers are complex : however these parameters are very important for the conception of pyrolysis unities.

4.2. Cinetic of pyrolysis in inert gas medium.

4.2.1. Adaptation of thermogravimetric technics.

T. ARAKI and Co (7) have made a preliminary study on the pyrolysis cinetic of commercial S.B.R. tyres pieces. They make use of a thermogravimetric method but don't precise the size of the sample. They have the heating speed varying from 1,25 °C/mn until 8° C/mn with the inert ga (nitrogen) flow speed of 10 cm^3/sec. It appears (figure 3), especially on the curves with a low heating speed, that the thermal decomposition is operated in two steps : the authors think that is the consequential to the presence of polybutadienewhich decomposes at lower temperature than polystyrene. D. BOUKADIR and Co (8) have studied by thermogravimetry, the pyrolysis of tyres crumb rubber (size of particles : 100 to 200 microns). From small samples (100 to 200 mg) and with constant heating speeds (1.15 to 2.3 ° C/mn), they also find two distinct stages in the degradation : the first phase, under 300° C, produces about 10 % of loss of weight and the second between 300 and 450°C, about 50 % of loss of weight. But they don't give precise detail about the nature of phenomena. The comparison with the previous results is difficult because the looks of thermograms are not similar, but the loss of weight is too low to be explained by the degradation of poybutadiene. These authors have also studied the cinetic of degradation in isothermal conditions, between 292° C and 337° C (figure 4).

From the standing equation :

$$\frac{d\,(\Delta P\,t)}{dt} = k\,(\,\Delta P_\infty - \Delta Pt\,)^n$$

where : ΔP_∞ is the loss of weight at equilibrium
ΔPt is the loss of weight at the instant t
k is the cinetic constant
n is the order

it is established that the order of the degradation equation is between 1 and 1.5 at low temperatures and increases until 3 at 337° C. However these studies don't give data at other temperatures and it is difficult to obtain a general conclusion.

More recently J.M. BOUVIER and Co have studied the pyrolysis of S.B.R. no with small milled samples but with bigger lumps (some mm^3 to some cm^3). They describe the influency of the temperature and the size of particles. By a thermogravimetric method especially adapted to dynamicaly weigh with control of temperature and gas composition of the medium.

The experimental line (figure 5) includes a vertical tubular furnace - 2 - able to produce and hold temperatures about 1 000° C. This furnace contains a quartz tube and is topped by a precision balance - 1 - which includes a sample holder - 3 - in the hot area. The sample receptacle has been conceived to avoid modifying thermal exchanges between the rubber and the furnace. An inert medium, is obtaining by regular flowing of nitrogen (2 to 5 l/mn).

The experimental procedure is the following :

- heating of the furnace until the designed temperature,
- feeding of the hot receptable,
- continuous recording of the loss of weight (figure 6).

All the recording graphs present the same shape : a first step where the loss of weight is important and a second phase which is an horizontal segment corresponding to the end of pyrolysis where charcoal residue and ashes remain.

4.2.2. Advancement graphs.

The thermograms have been transformed into pyrolysis reaction advancement graphs x = f(t) where x is the conversion rate defined by :

$$x = \frac{p_i - p_t}{p_i - p_f}$$

p_i is the starting mass of the rubber sample,
p is its mass at instant t,
p_f is its mass at the end of the pyrolysis, i.e. the mass of the charcoal residue.

Figure 7 presents the advancement graphs at diff rent temperatures (from 315° C to 525° C) for constant cubic geometry samples (sides of 5 mm). This small size allows all the mass of rubber to quickly reach the isotherm running.

These curves show three distinct fields :

- The minus 315° C temperatures field : where the loss of mass is only explained by the volatilization of the extension oil and the mass of solid residue at equilibrium decreases with the increasing temperatures.

- The 315-430° C temperatures field : which presents two parallel phenomena : the physical volatilization of the extension oil and the chemical thermal degradation. The pyrolysis reaction is very slow at low temperatures but its speed draws nearer to the volatilization cinetic if the temperature increases.

- The more 430° C temperatures field where the pyrolysis reaction is fast and hides the whole volatilization process as soon as the temperature reachsto 450° C. The whole elastomer is pyrolysed and a charcoal residue (34-37 %) remains, including the initial carbon black, a part of the sulphur, and a mixing of sulphur and zinc oxide.

Likening the physical volatilization to a chemical process, the authors have identified the cinetic parameters of the two observed phenomena to design a global behaviour model of the speed of the thermal degradation of vulcanized S.B.R.

The advancement graphs have a sigmoïdal shape because of the shortness of the thermal induction stage at the beginning of the degradation So, considering only the isotherm part of curves, from the inflexion point, the authors have determinated the cinetic parameters of the two processes (table 4).

Temperature of thermal degradation °C	Volatilizing process	
	order (n)	speed constant ($K_1.10^2$ mn^{-1})
326	2	5
343	2	10.2
353	2.09	13.1
361	1.71	22.8
	Pyrolysis process	
372	0.86	1.25
402	1.04	4.16
424	1.11	15.26
466	1.04	222.6
502	1.11	338.7
525	0.94	575.5

TABLE 4 - Cinetic parameters of volatilizing and pyrolysis processes versus temperature (9)

These parameters show that the volatilization process looks like a reaction of order 2 but it is the simple simulation of a diffusional process : the starting point of the extension oil is near to 220° C, i.e. under the pyrolysis temperature ; when the temperature increases, this oil is eliminated by diffusion inside of the rubber and the phenomena is distinguished by a pseudo 2 order reaction : this result has already be observed with regard to the elastomers inflating (10, 11). The pyrolysis process looks like a first order reaction, as seen in anterior works. The activation energy is 43 100 cal $mole^{-1}$ and the frequency factor is $3{,}9 \, . \, 10^2$ mn^{-1}.

From these data, models of the global pyrolysis speed of S.B.R. versus temperature and conversion rate can be established :

. $T < 350°$ C $\quad Vp = (9.2 \times 10^{10} \exp - \frac{17\ 000}{T}) \; (1 - x)^2 \; mn^{-1}$

. $350° \text{ C} < T < 470° \text{ C}$:

$$vp = (1.6 \times 10^{10} \exp - \frac{17\ 000}{T})(1 - x)^2 + (3.9 \times 10^{12} \exp - \frac{21\ 800}{T})(1-x) \text{ mn}^{-1}$$

. $T > 470° \text{ C}$: $vp = (3.9 \times 10^{12} \exp - \frac{2\ 180}{T})\ (1 - x) \text{ mn}^{-1}$

This model must be carefully interpreted because the value of cinetic parameters depend on the experimental procedure and the treatment of results. Estimations of activation energies and frequency factors may greatly vary. The global reaction is the resultant of a great number of elementary reactions. This model is founded on the hypothesis of an isotherm running which is valid in the case of small size samples.

This model is representative of a chemical rate of pyrolysis. In the goal of an industrial full scale utilization of the pyrolysis, it is necessary to study the part of the samples size : at which temperature the thermal rate takes the place of the chemical rate ? This question is very important to adjust the industrial technology and to optimize the mechanical pretreatment or shredding of the waste.

4.2.3. Effect of temperature and sample size upon the pyrolysis time.

If the total pyrolysis time tp is defined as the time necessary to obtain a conversion rate $x = 0.9$, it is possible to study tp versus the temperature (figure 8). Greater the sample size, longer the time tp : by example, at 500° C tp = 100 s for 5 mm side cubic sample. At lower temperatures, tp decreases very quickly in a first stape, then the decreasing becomes slower and linear, especially for more important size samples. This behaviour shows that the thermal degradation cinetic is limited by the thermal transfer. For a given particle geometry, the pyrolysis cinetic is determined by the surface temperature of the sample : it is the thermal rate. If the pyrolysis is governed by heat transfer inside the material, the main parameter regulating this conductive transfer is the Fourrier number (F).

$$F = \frac{\alpha\ t_{DT}}{D^2}$$

α : diffusity number
t_{DT} : thermal diffusion time
D : characteristic dimension.

The number F' obtained by substituting for t_{DT} the pyrolysis time tp, is representative of the thermal transfer of the global pyrolysis.

If the pyrolysis is limited by the thermal conductive transfer, F' is constant and there is a linear relation between the pyrolysis time and the square of the dimension (cube side), as it is shown in figure 9 at more 460° C temperatures. At minus 460° C temperatures, the pyrolysis is probably regulated by the thermal decomposition cinetic, especially for small size samples. At higher temperatures, the surface temperature of the rubber (quickly at the equilibrium with the furnace) governs the pyrolysis speed : the pyrolysis process is limited by the thermal transfer inside of the rubber. The slope of the obtained graphs corresponds to the ration F'/α. F' is constant and the thermal diffusivity of the rubber increases with the temperature.

Except for the case of the pyrolysis of crump rubber, these results show that the pyrolysis process is limited by the thermal transfer because of the size of materials. At industrial scales, these considerations on the fluid-rubber thermal transfers will be important.

In fact, these results show that the pyrolysis time, above 500° C, is relatively short and the pyrolysis of whole tyres seems possible : their contact surface is important enough and no greatly increased by shredding : the tickness of car tyres is near to 2 cm. But a gas-solid contact is not the best way of heat transfer, in comparaison with a liquid-solid transfer which is more efficient. From this consideration, the team of Compiegne University has developed an original pyrolysis process, including a thermal degradation in a solvent liquid medium.

4.3. Cinetic of the solvent liquid medium pyrolysis.

The thermal treatment is operated in presence of a liquid. Contrary to pyrolysis in smelted salts medium the main function of which is the heat transfer, here, the liquid realizes the double job of heat bearer and solvent for the elastomer degradation products. This solvent must be thermally stable and will be chosen in regard of the balance between its chemical properties and its price. Its structure will be compatible with the elastomer and its vapor pressure will be low enough to allow the tranformation and the atmospheric pressures. Heavy hydrocarbons suit perfectly to this utilization.

4.3.1. Influence of the temperature and the sample size in solvent liquid medium.

Table 5 shows the fundamental influence of the temperature. The total dissolution time decreases from 150 hours until few minutes when the temperature increases from 200° C to 360°. Two phenomena govern the dissolution process : the diffusion and the thermolysis. They are competing according to the temperature. At low temperatures, only the sulphur vulcanizated macromolecules become soluble because of the breaking of the carbon-sulphur interchain linkages. If the vulcanization has producted only carbon-carbon linkages (peroxide vulcanization) the tridimensional structure remains insoluble. At these temperatures, the macromolecules dissolution, i.e. the elastomer-solvent diffusion, is the limiting phenomena. Above 200° C, the carbon-carbon linkage can break and the craking speed increases with the temperature and shorter chains are producted and able to be easily dissolved ; at high temperature it is the chains breaking reaction which regulates the process. An experimental test confirms this theory : a sulphur vulcanized S.B.R. sample is immersed in a aromatic hydrocarbon at ambiant temperature until the inflating equilibrium (increasing of 79 % of weight by oil absorption). After this treatment the sample is heated by immersing in the same hot solvent : the whole sample is dissolvedin one hour at 260° C, 11 minutes at 280° C. If there is no preinflating treatment, the sample is only dissolved after 15 h 30 mn and 2 h 50 mn at these temperatures where the limiting process is the molecules solvatation.

Temperature ° C	200	220	240	260	280	300	320	340	360
Total dissolution time	150 h	57 h	28 h	15.5h	2.8 h	42 mn	26 mn	12 mn	7 mn

TABLE 5 - Total dissolution time of a 1 cm diameter S.B.R. (sulphur vulcanized) sphere, immersed in an aromatic heavy oil (11).

The nature of the solvent is an important parameter : if a paraffinic hydrocarbon is used in place of the heavy aromatic hydrocarbon, the total dissolution time increases at 320° C from 26 minutes to 5.75 hours. But this difference decreases quickly with the temperature increasing and becomes zero near to 380° C. However, the solvent activity of an aromatic hydrocarbon for the S.B.R. and natural rubber is greater : it is another important parameter, i.e. the ratio oil/rubber. In the case of the S.B.R. aromatic hydrocarbon couple, the critical value of this ratio is about 1.5 and 2. Above this value, the total dissolution time is constant and under this value, the solid remains pasty and its structure is damaged. It is a demixing phenomena producing a diluted phase, including dissolved light polymers and a concentrated phase upgraded with heavy polymers.

The sample size effect is important at low temperature but decreases quickly with its increasing. At high temperatures the advantage of particles reducing is minor. It seems possible to dissolve big pieces and whole tyres.

4.3.2. Advancement graphs.

Solvent medium pyrolysis follows from complex physico-chemical processes. The global cinetic results from a competition between the diffusion and the chemical reactions, but the mechanism involves a big varying of the solid caracteristics, depending of the transformation advancement. From the experimental data, it seems possible to distinguish two steps : in the first step, the solid is inflating by diffusion of the oil in the vulcanized structure. In the second step, the structure is degrading and dissolving. So, the advancement rate of this pyrolysis cannot be founded on a weight criterium (low of weight, by example) because of the inflating step. But rubber includes carbon black and the pyrolysis conversion rate can be determinated by the carbon black freeing rate (method elaborated by F. FARHADI (13)).

The advancement graphs (figure 10) show the quick degradation at more 350° C temperatures. Though the thermal induction time is not figured (the origin point is the beginning at the isotherm area), curves have a sigmoïdal shape. It is a particular behaviour near to auto catalytic systems with germination, or phases changing models. The description of phenomena is not well known.

In a first time, the authors have submitted a model representing a first order reaction : so, the reaction speed follows the formula :

$$\frac{dx}{dt} = \sqrt{(t)} \quad [\ 1-x\ ]$$

$\sqrt{(t)}$ is a function which becomes constant when x is so high enough.

An analytic formula may be :

$$\sqrt{(t)} = \gamma\ .\ [\ 1 - (1 + t^{*}) \quad \exp - t^{*}\ ]$$

t^{*} is the time under an adimensional form. The global cinetic constant γ. (table 6) follows the Arrhenius law between 330 and 360° C, that allows to deduce the values of the frequency factor $-7.8 10^{19} s^{-1}$ - and the activation energy - 64 Kcal $mole^{-1}$ - .

Temperature ° C	360	350	340	330	320
$\gamma\ .\ 10^{2}$, mm^{-1}	48	16	5	2	1.7

Table 6 - Total speed constant versus temperature.

But this model doesn't permit the interpretation of the experimental curves but shows that the reaction has a first order cinetic after the inflexion point. The authors have tried to explain the autoaccumulation of the reaction before this point.

The cinetic constant is very higher when the thermolysis is operated in liquid medium. In gazeous medium, the conversion rate is limited by the volatilization rate of polymer fragments but in liquid medium, it is function of their solubility in the liquid. That is why the conversion in gaseoux medium supplies in light molecular weight products and, in liquid medium, high molecular weight products.The ratio of cinetic constants is mainly depending of the solvent activity of the medium hydrocarbon. The macromolecular chains are surrounded by solvent molecules producing at these temperatures, radicals hydrogen especially (H°). These radicals fill up the active sites and radicals of macromolecular chains produced by thermal initiation.

By this fact, as the molecular mass of the initial polymer is very hight, about 10^5 to 10^6, the likelihood to obtain soluble oligimers is low at the beginning of the process and gradually draws near to 1. That explains the sigmoïdal shape of degradation curves and, into the classic equation of first order reaction it is necessary to include an adimensional paramater P :

$$\frac{dx}{dt} = kP\,(1 - x) \quad 0 \leqslant P \leqslant 1$$

P is the probability to obtain soluble oligomers in the thermolysis liquid medium ; it depends on x :

P = 0 when x = 0

P = 1 at the inflexion point of the curve.

The authors have determinated the theoric value of P, supposing that the thermal initiation process of macromolecular chains is statistic and not followed by recombination reactions (10).

The experimental values seem credit this theory on the solvent medium pyrolysis of S.B.R.

The knowledge of the cinetic paramaters is very important to ajust the operating conditions and a reliable technology but is not suffisant to justify the use of pyrolysis in the beneficiation of rubbers and tyres. It is necessary to know the nature and the quality of products resulting of this beneficiation to appreciate the economic balance of the process.

5. PYROLYSIS PRODUCTS.

5.1. Nature of the pyrolysis products.

It's the U.S. Bureau of Mines who has been the first to study the pyrolysis of rubber making a destructive distillation by heating the rubber at high temperature until such time as the gazeous flow is very low. The recovered products are gas, liquid, an solid, the quantities of which very according to the temperature (table 7). The increasing of the temperature promotes the gas production. Other parameters - nature of tyres, conditionning of samples (crumb or pieces) have no effect upon these rates.

temperature ° C	Types of tyres	Rate, weight %				
		residue	light oil	heavy oil	gaz	total
500	car	42	45.2	4.2	5	96.1
900	car	52.3	14	6.5	20.8	93.6
500	lorry	36.5	48.7	4.3	5	94.5
900	lorry	55.2	17	5	19.2	96.4

TABLE 7 - Rate of pyrolysis by simple destructive distillation (2)

A. LUCCHESI and G. MASHIO (19) obtain the same results in studying the pyrolysis of shredded car tyres. This pyrolysis has been carried out in a tubular furnace fed by a flow of nitrogen or carbon dioxide, between 400° C and 700° C. They establish that the gas production increases and the oil production decreases when the temperature is increasing : at 700° C the gas rate and the oil rate reach to the same value (32 % in weight)(figure 11). In this temperature field the carbonaceous residue rate is constant.

The obtained gas has a high hydrogen content (55-54 %) with methane (9-25 %), ethane (22-13 %), propane (8-21 %). These values are expressed in volume for temperatures between 500° C and 900° C.

Its calorific value is approximatively 8 300 Kcal/Nm^3, i.e. like the natural gas.

The analysis of heavy oils is not easy because they are the mixing of more than one hundred compounds.

The solid residue is a carbonaceous product : it mainly contains char (∿ 85-90 %), sulphur (2 %), ashes (8-13 %) and its calorific value is near to 7 500 Kcal/kg.

A similar study (15) realized between 500° and 600° C in a 100 liters reactor loaded with cut used car tyres, has given a lightly different rate (table 8).

Pyrolylis products 500-600° C	Rate, weight %
. Solid : iron scrap	12.4
carbonaceous residue	37.6
. Liquid : water	3
oil	33.8
. Gaz	6.4
TOTAL	93.2

TABLE 8 - Average weight composition of pyrolysis products from a 100 l - Pilote unit (15).

In the case of solvent medium pyrolysis, the temperature is lower and the gas production small. The average weight balance (except iron and textiles) is the following :

. gas : 5 %
. liquid : 60 %
. solid : 35 %.

The solid residue is in suspension inside the liquid. Temperature does not alone influence these rates. Technology is another parameter which will be developed in following items. It can be here mentioned average balances resulting of industrial pilot scall processes (table 9). It appears logically that the technologies optimizing the heat transfer produce a more important craking of the hydrocarbonated materials.

Process	Pyrolysis temperature°C	Pyrolysis products, weight %		
		gaz	liquid	solid*
Solvent medium	360-380	∿ 5	∿ 60	∿ 35
Tubular bilan + Archimede screw	430-450	13	37	50
Relative bilan (Tosco)	480	6	61	33
Relative bilan (Kobe-steel)	550	6	57	37
Fixed counter flow bed	660	12	50	38
Fluidized bed (Reprox)	} 450	17	48	35
	550	23	45	32
Fluidized bed (DRP)	700-750	25	31	44

* excluding iron scraps and textiles

TABLE 9 - Composition of pyrolysis products versus technologies.

All the pyrolysis products can be used as fuel but to optimize the economic profitability, it is necessary to consider more elaborate beneficiations with intent to recycle or utilize these products like raw materials of the chemical industry. Then it is necessary to well know their production qualities and constancy to look to their potentiel market.

5.2. Characteristies and uses of pyrolysis products.

5.2.1. Gas.

The pyrolysis temperature does not influence the gas composition but the production of unsaturated compounds (ethylene, propylene and even butadiene - 1,3) is promoted in inert gaseous atmosphere(table 10). In the case of the liquid solvent medium pyrolysis the hydrogen production is negligible. On the other hand, the butene production is very hight because of the craking of the basic elastomer polybutadiene. The thermal degradation produce radicular hydrogen which, in liquid solvent medium, because of the transfering effect of the hydrocarbonated oil, saturates olefins and does not combine.

The gas composition depends also on the contact medium : in lightly oxydant medium, the ratio of Co and CO_2 can be relatively important : it remains minus to 3 % in anaerobic medium.

The pyrolysis gaz has a very high calorific value, generally between 800° C and 10 000 $Kcal/Nm^3$. It is used like fuel, as often as not to produce the energy of the pyrolysis unit.

5.2.2. Liquid.

The rubbers and tyres pyrolysis produces very miscellaneous molecular weight molecules because the elastomer depolymerisation responds very likely to the controls of a statistic process. Of course high temperaturespromote a lower average molecular weight, as shown in the study of A. LUCCHESI and G. MASCHIO (19), operated in a tubular furnace fed by a flow of nitrogen or carbon dioxyde (table 11). However the nature of the bearing gas does not

Components weight %	Laboratory pyrolysis of car tyres (tubular kiln with Nitrogen flow 750° C) (17)	Half industrial pilot pyrolysis of car tyres (fludized bed, 700° C) (18)	Liquid solvent medium pyrolysis at 380° C (16)	
			aromatic oil +	
			car tyre	Public works engine tyre
H_2	2.7	2.4	-	-
CH_4	30	35	23	22.6
C_2H_4	22.9	9.5	1.9	1.8
C_2H_6	11	13.5	10.2	8.3
C_3H_6	13.8	8.8	5.1	5.7
C_3H_8	2.2	2.5	10.3	10.7
C_4H_6	5.8	1.5	-	-
C_4H_{10}	-	-	8.3	10.2
CO	undertermined	8.5	3.6	1.6
CO_2	undertermined	10	3.7	2.1
H_2S	undertermined	0.1	10.4	10.7

TABLE 10 - Pyrolysis gas composition versus reactional medium.

influence the distilling curve. But it is important to note de desulphurizing effect of CO_2. From Y. SAEKI and G. SUZUKI (20), the sulphur content is more important in heavy molecular weight fractions. The molecular ratio H/C is 1.5, that is why the oil has an important aromatic trend. This result is confirmed by N. KAMINSKY and H. SINN (18, 21-23) who have obtained, at semi-industrial scale at 700-750° C, an aromatic compounds rate superior to 20 % of the rubber weight, i.e. 60 to 70 % of aromatic compounds in the liquid phasis. They state that the pyrolysis reaction follows two steps : in the first stape, macromolecular are decomposed in light weight unsaturated molecules ; in the second stape, these molecules react each with another to produc aromatic compounds, methane and hydrogene. This second step is promoted by increasing of the temperature and residence time.

R. CYPRES and B. BETTENS (17) have studied thoroughly the short chain olefines aromatization, using a pyrolysis in a tubular furnace at 400-450° C followed by a post-craking in a isothermal furnace at 600-800° C. The analysis of curves (figure 12) shows an upgrading of aromatic fractions when the post craking temperature increases. This aromatization is obtained from short chain olefines (ethylene, propylene) by deshydrogenation and cyclisation of the liquid phase components. An hydrogen richer mixing of gases results.

Pyrolysis conditions		Distillation, weight %			$\overline{Mn}$	Sulphur content weight %
Temperature ° C	gaz flow	60-200° C	200-275° C	275-395° C		
500	CO_2	16.5	10.7	31.2	200	0.2
600	CO_2	22	9.4	36.3	190	
700	CO_2	37.3	11.8	26.6	135	
500	N_2	14.7	11.3	37	220	0.6
600	N_2	29.3	12	26.7	157	
700	N_2	38	12.8	19.2	128	

$\overline{Mn}$: average molecular mass in number

TABLE 11 - Characteristics of distillation of the pyrolysis oil versus temperature and gas flow (19).

The authors have also studied the influency of γ irradiation on the hydrocarbons rates and the aromatic hydrocarbons nature, especially light molecular weight products. The irradiation tends to reduce the aromatic fractions and increase heavier compounds. An increasing of the residence time in the second furnace promotes the polynuclear compounds formation. The short chain olefines aromatization is realized by Diels-Alder reactions, by example :

cyclohexene

methyl-4 cyclohexene-1

vinyl-4 cyclohexene-1

octohydronaphtalene

The 6 carbons cyclic compounds give by deshydrogenation, the corresponding aromatic products. By later connecting reaction, polycyclic compounds may be produced.

If the pyrolysis is operated in heavy hydrocarbon medium (16), the liquid phase includes a light fraction with an initial point at 73° C and a final point at 194° C (sulphur content : 0.6 to 0.8 %) and an heavy oil corresponding to the contact oil mixed with degradation oligomers, and the carbon black in suspension (table 12). It is shown that the oil viscosity decreases after pyrolysis because of the fluxing effect of light fractions.

Characteristics of the heavy oil before and after pyrolysis	Aromatic extract		Heavy fuel oil n° 2	
	alone	+ rubber	alone	+ rubber*
Volumic mass at 26° C, g/cm^3	0.998	1.019	0.984	1.007
Viscosity at 50° C, Cst	300	266	362	223
Flowing point, ° C	+27	+3	0	3
Conradson carbon, weight %	2.2	9.3	13.7	18
Sulphur, weight %	4.9	3.88	3.7	3.14
Zinc, weight %	-	0.32	-	0.48

* heavy oil extracted from car tyre in semi-industrial unit.

TABLE 12 - Characteristics of the heavy oil produced by liquid solvent medium pyrolysis. (T = 380° C, ratio oil-rubber : 3) (16).

The Conradson carbon increases because of the presence of carbon black in suspension. The sulphur contents decreases lightly and zinc inserted with the rubber appears in the form of zinc oxide.

5.2.3. Solid.

The solid residue is a very important part of the pyrolysis products, about 35 % to 40 % of the weight of rubber or tyres. Its weight does not depend of the temperature, but its composition is more sensible (table 13). It has a high carbon content because of the important presence of carbon black in the rubber. It includes also the main part of the sulphur and zinc incorporated in the rubber (crosslinking and vulcanizing agents). Because of its calorific value, this carbonaceous residue can be used like fuel after recovery of iron scraps ; but it seems necessary to consider more interesting valorizations to have a better profitability of processes, especially when their technology is complex and expensive.

Analysis of the carbonaceous residue, weight %	Pyrolysis by fluidized bed REPROX Process(20)	Pyrolysis by fixed bed	
		500° C	900° C
Global analysis			
water	0.7 - 0.8	0.7	0.2
volatiles	4.8 - 8.6	3.4	1.0
fixed carbon	82.4 - 82.7	86.3	90.5
Elementary analysis			
carbon	85.6 - 88.0	86.5	90.2
hydrogen	0.03 - 0.68	1.3	0.5
ashes	8.36 - 11.8	9.6	8.3
sulphur	2.22 - 2.24	2.0	1.7
zinc	47 - 5.1	-	-
Law calorific value kcal/kg	7120 - 7650	7490	7510

TABLE 13 - Composition of the cabonaceous residue versus pyrolysis temperature.

Three valorizations can be developed according to its physico-chemical properties :

. as strengthening charge for the rubbers or plastics making,

. as raw material for the activated carbon making,

. as a source of recoverable zinc.

5.2.3.1. Utilization of the residue as strengthening.

Reuse of the carbonaceous residue depends of the evolution of its physico-chimical properties during the pyrolysis treatment. In comparison with the virgin carbon black, its mineral elements content is upgraded and its properties may be have been modified by its rubber inserting treatment, by the conditions of the vulcanizated rubber use and pyrolysis.

The strenghtening activity of the carbon black inside a rubber depends on the elastomer accessibility to the particle surface and the creating of polymer-charge linkages. So, the specific area, pore-dimension, surface activity and structure of the carbon black, influence its strenghtening quality.

G. PONCELET (24) has shown that during the inserting of the carbon black into the vulcanizate, a part of the aggregates are destroyed. Moreover, a part of the rubber is very strongly bound to the black. The recovered carbon black will present smaller specific area and surface activity what ever the rubber pyrolysis process may be. A carbon black, recovered from a pyrolysis treatment of waste , will be always less strenghtening because its physicochemical properties are changed during the rubber making. However, this study, operated with a carbonaceous residue produced by a solvent medium pyrolysis at 380° C, does not permit a general estimate, especially for the carbon black coming from hight temperature pyrolysis.

In other reports, S. KAWAKAMI and Co (25) have shown that the strengthening properties of the black are maximum at 600°C and after, decreasing when the temperature increases. They explain this decreasing by a bad scattering of the black inside the rubber, because of an increasing of the cohesion strenght between the carbon black particles.

At high temperatures, a part of the carbonaceous residue, coming from decomposition of oil and gas, makes the cohesion strengths so strong that the aggregates cannot be broken : this recovered carbon black is difficult to be reused. Some authors have tried to optimize the quality of the carbon black by different technics (hot chlorhydric acid treatment, thermal retreatment, mechanical treatment), but its qualities remain very insufficient. It is difficult to present here the physico-chemical properties of carbon black obtained by differents authors. They have only a relative value because their determinations are not standardized and because the commercial carbon blacks (HAF, FEF, GPP) have very varying properties.

It can be generally observed that :

- The size is identical with the original carbon black's one.
- The DBP index is always lower, what shows a degradation of the structure.
- The specific area and the microporosity decrease and an important macroporosity appears.

It seems that a high quality black (HAF) behaves, after vulcanizing and pyrolysis of the vulcanizate, like a middle quality black (GPF : semi-strengthening) that is why the vulcanized rubber charged with a carbon black recovered by a pyrolysis process present generally lower rupture strength and modulus but an almost identical lengthening and tearing strength (table 14).

After solvent medium pyrolysis, the carbon balck extracted from the oil, bears an important quantity of no transformed sulphur and zinc oxide. Thereby these constituents produce an "over-vulcanizing" including an higher modulus and a lower lengthening. This process may open an other way of recycling : the pyrolysis product is a suspension of carbon black in heavy oil and can be completely recycled and serves as a substitute for extender oil and carbon black. By example, the basic elastomer of wind-screen joint is a sulphur vulcanized DEPR (EDPM(S)) and the one of fexible connection coupling is a peroxide vulcanized EPDM (EPDM(P)). Corresponding waste has been pyrolysed at 380° C in presence of the extender oil of the elastomer which is used as solvent medium. By recycling the whole produced heavy oil, its carbon black and degradation oligomers content increases : a light decreasing of the vulcanizate properties can be observed (table 15). The dynamometric properties are less good and the lengthening more important. The hardness is less good but the tearing strength is well increased. In comparison with the reference sample, the vulcanizing speed is increased, except in the case of the recycling of the EPDM(P) suspension. This logical result is obtained by the presence of sulphur, zinc oxide and accelerators in the suspension. The dynamometric

Mechanical propertises of vulcanizates*	Pyrolysis at 380 ° C (24)		Pyrolysis at 600° C (25)		Pyrolysis at 900° C (14)	
	Reference (HAF)	Pyrolysis black	Reference (GPF)	Pyrolysis black	Reference (HAF)	Pyrolysis black
Rupture strength, MPa	27.3	22.3	28.1	25.9	19.6	17.9
Modulus 300 %, MPa	13.2	15.9	19.9	14.7	13.3	10.9
Lengthening, %	538	377	400	440	400	440
Tearing, daN/cm^2	49	37	39.2	34.3	-	-
Hardness- DIDC	69	74	69	67	-	-
* used formula include 1502 SBR, sulphur-vulcanizing						

Table 14 - Mechanical properties of vulcanizates including a carbon black produced by tyres pyrolysis.

properties obtained with the EPDM (P) suspensions are better, likely because of the presence of suphur, zinc oxide and acceleration which keep during the thermolysis.

This difference seems to indicate an "under-vulcanizing" in the case of the recycling of the EPDM (P) suspension : during the mixing and the vulcanizing, a shortage of sulphur may appears when the usual quantities are added. The sulphur would be used up by double residual linkage reactions in the degradation oligomers melted in the solvent. The values of the iodine index (table 16) back up this interpretation. The EPDM (S) suspension presents indeed an very higher iodine indice than original elastomer and extender oil (Plaxene oil 6110). This insufficient vulcanizing reduces the mechanical properties. The increasing of the tearing strengths, especially with the EPDM (P) suspension, issues likely from the presence of higher weight oligomers than the extender oil.

Formula	Reference	Sample
EPDM elastomer	130	130
FEF carbon black	150	130
6110 Plaxene	80	40
Recycled suspension*	0	60
Zinc oxide	5	5
Stearic acid	1	1
Sulphur	2	2
MBT	1.5	1.5
DTMT	0.8	0.8
Tellurac	0.8	8

Mechanical properties		suspension origin	
		EPDM (S)	EPDM (P)
Rheomètre t90, 160° C	9'	7' 45"	10'
Rupture strength, MPa	11.4	11.6	12
Modulus 100 %, MPa	3.9	4.4	3.0
Modulus 300 %, MPa	10.0	10.5	8.8
Lengthning, %	350	360	470
Tearing, daN/cm^3	29	28	37
Hardness DIDC	73	73	69

* rate of waste recycling : 5.4 weight %

Table 15 - Mechanical properties of vulcanizates after recycling of a suspension of carbon black in solvent medium pyrolysis oil (11).

Sample	Iodine index
Original EPDM	118
Plaxene 6110 (extender oil)	33
EPDM (P) suspension	172
EPDM (S) suspension	169

Table 16 - Iodine index of original materials and recycled suspensions (11)

These results show that the recycling is possible but the better way is the recycling of a suspension inside a same type compound because of the chemical compatibility. It would be necessary to optimize the recycling rate and the proportion of cross-linking and accelerating products in order to find again the same properties as the reference samples.

The charcoal residue can also be incorporated into thermoplastics (polyethylene, polypropylene, polystyrene, PVC...). This possibility has been investigated by J.M. VERGNAUD and Co (26) : they have studied the incorporation of a partially pyrolysed fine crumb rubber (200 to 500 microns) into a low density polyethylene (the pyrolysis has been run at low temperature : 300 to 320° C). The results (table 17) show that the recycled crumb rubber has the same behaviour as SRF carbon black, principally when the less of mass is important ; it is well spread inside the polymer matrix. Lastly, it gives to the plastic material a better resistance against the U.V rays.

Nature of the charge : pyrolysis rate described by the loss of weight %	Rupture strengh daN/mm^2	Modulus daN/mm^2	Lengthening %	Hardness
28	1.3	6.9	150	98.2
34	1.32	7	153	98.2
51	1.38	7.1	153	98.3
61*	1.42	7.2	172	98.3
SRF carbon black	1.40	7.4	168	98.4
pure polyethylene	1.30	6.6	260	97.9
* total pyrolysis				

Table 17 - Mechanical properties of polyethylene (95 %) charge (15 %) mixing, versus pyrolysis rate of the charge.

5.2.3.2. Utilization of the carbonaceous residue as raw material in the activated carbon making.

The specific area of the carbonaceous residue increases with the temperature ; it is more important when the pyrolysis is operated in presence of CO$_2$ (table 18). Though the obtained values, even at high temperature (700° C) are very lower than the commercial activated carbons, the pyrolysis charcoal presents a very good adsorbent power, after better than the commercial ones (figure 13). By the black acid colouring, its adsorbent power is 4 or 5 times higher than the commercial charcoal characterized by a specific area of 1 000 m^2/g. R. CYPRES and B. BETTENS (17) have stuedied the adsorbent properties of an activated pyrolysis charcoal residue. It is actived by water steam at 960° C during 30 minutes. The losses of weight of the charcoal are about 30 to 40 %. The figure 14 presents the adsorption isotherms of phenol on a commercial activated charcoal and some charcoals produced by pyrolysis at different temperatures. It can be seen that the charcoals obtained at 550, 600° and 700° C have adsorbent qualities near to commercial charcoal ; the better is the charcoal obtained at 550° C.

Pyrolysis temperature, °C	Specific area, m^2/g	
	Na flowing gas	CO_2 flowing gas
500	210	270
600	320	380
700	350	570

Table 18 - Effect of the pyrolysis temperature and the nature of flowing gas on the carbonaceous residue specific area (19).

5.2.3.3. Utilization of the carbonaceous residue as source of raw material for zinc recovery.

Among the raw materials included in the carbonaceous residue, zinc is an important part, about 4 to 6 % in weight. Its extraction may be considered as valorization way.

F.C. HAAS and M.M. GUTIERREZ (27) have studied a recovery method in presence of chlorine or chlorhydric acid, at 750-1 000° C, allowing to convert the zinc oxide into gaseous zinc chloride. By the way, the authors affirm that they are able to realize an extraction with a efficiency better than 99 %.

6. CONCLUSION.

Because of the presentation of the materials to treat, the pyrolysis of old rubbers and tyres, operated in inert gas atmosphere, is governed by heat transfer when the temperature is above 460° C : in this case it is important to adapt the technology optimizing the heat transfer. If the temperature is below 460° C, the pyrolysis is more depending on the cinetics of thermal decomposition reactions and to speed up the global degradation process of materials, a solvent of oligomers of rubber degradation can be used.

There are three pyrolysis products : a gas, a liquid and a solid. Their respective percentage depends mainly on the pyrolysis temperature.

The gas is generally burnt on the site.

The liquid, inclined to an aromatic composition may also produce energy with possibilities of storage and transport. The solid, alone, a carbonaceous residue, can be valorized better than by energy recovery. Though its properties are lower, its recycling is possible, especially in middle quality making. The solvent medium pyrolysis gives the supplementary avantage of the simultaneous recycling of the oil and the carbonaceous residus.

The reutilization of these products can be optimized yet, but depends on the state of the art of the processes technology.

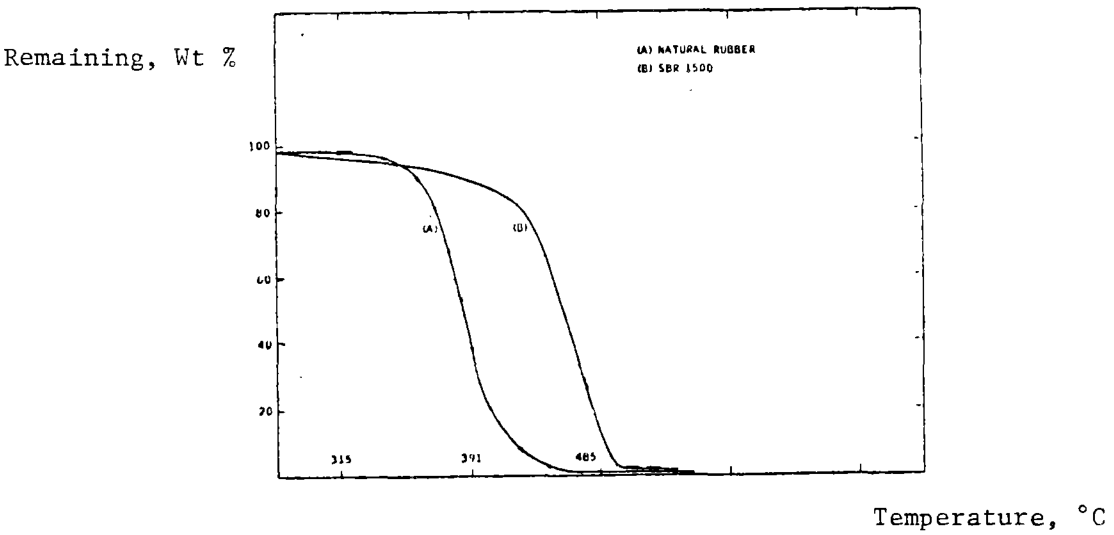


Figure 1 - Thermal stability variation of SBR and natural rubber.(4)

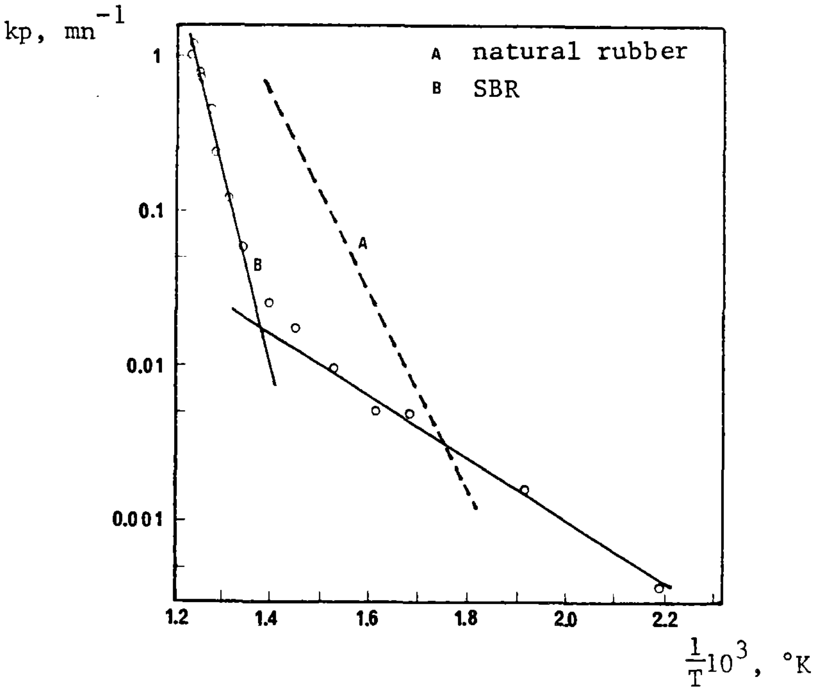


Figure 2 - Arrhenius plot for SBR 1500 and natural rubber.(5)

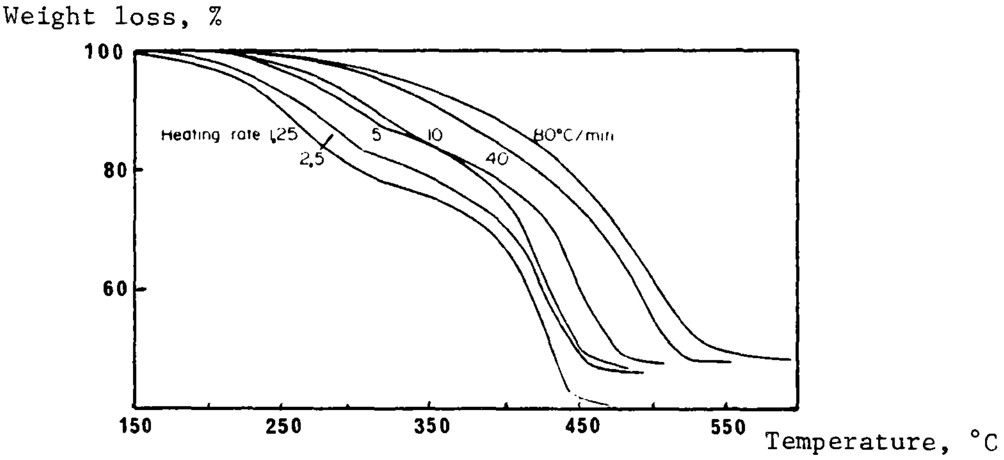


Figure 3 - Thermogravimetry curves of tyre chips in N_2 stream of 10 cm/s.(7)

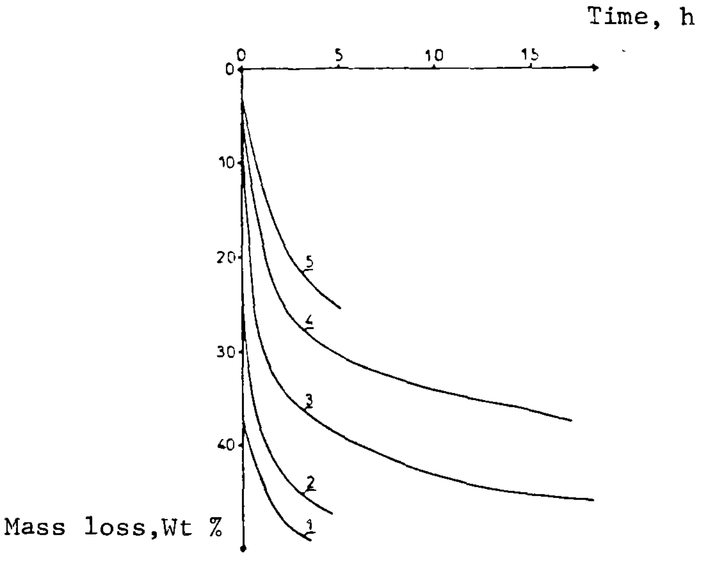


Figure 4 - Thermograms of thermal degradation of powdered tyres under oxygen free and isothermal conditions (1 : 337°C ; 2 : 329,5°C ; 3 : 308,5°C 4 : 302,5°C ; 5 : 292°C).(8)

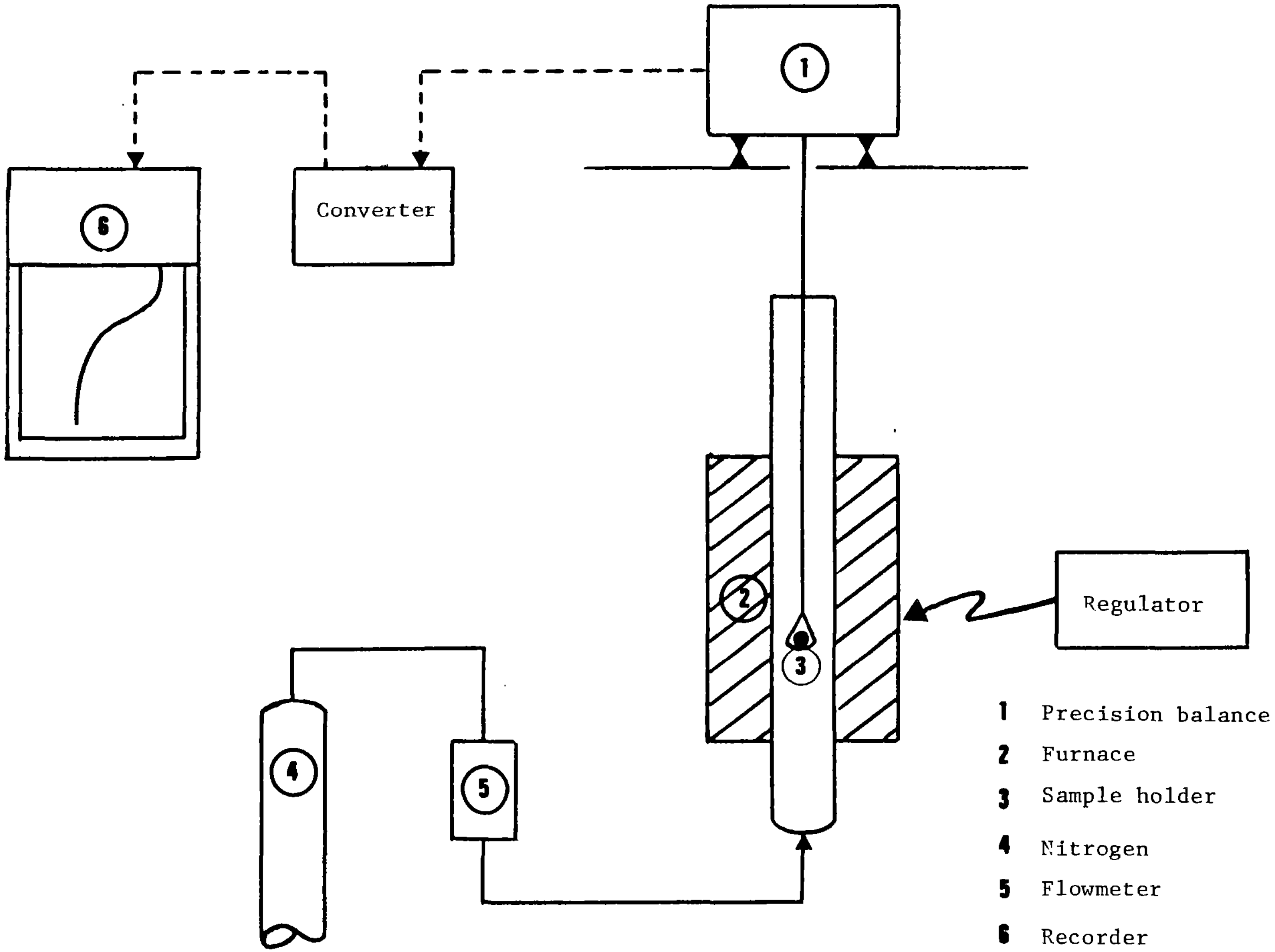


Figure 5 - Pyrolysis apparatus in inert atmosphere .(9)

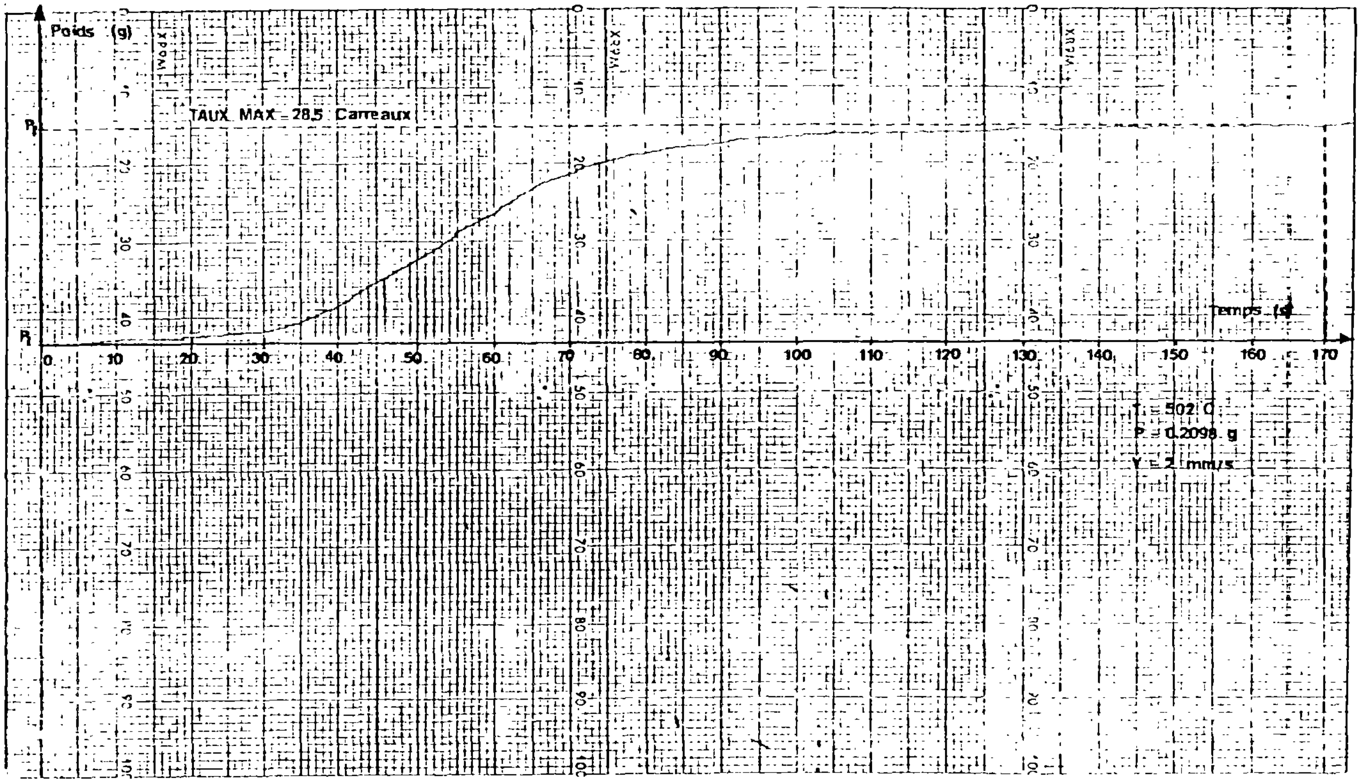


Figure 6 - Pyrolysis thermogram of cubic sample (initial mass : 0,21 g) from tyre under isothermal conditions (502 °C) and inert atmosphere (nitrogen).(9)

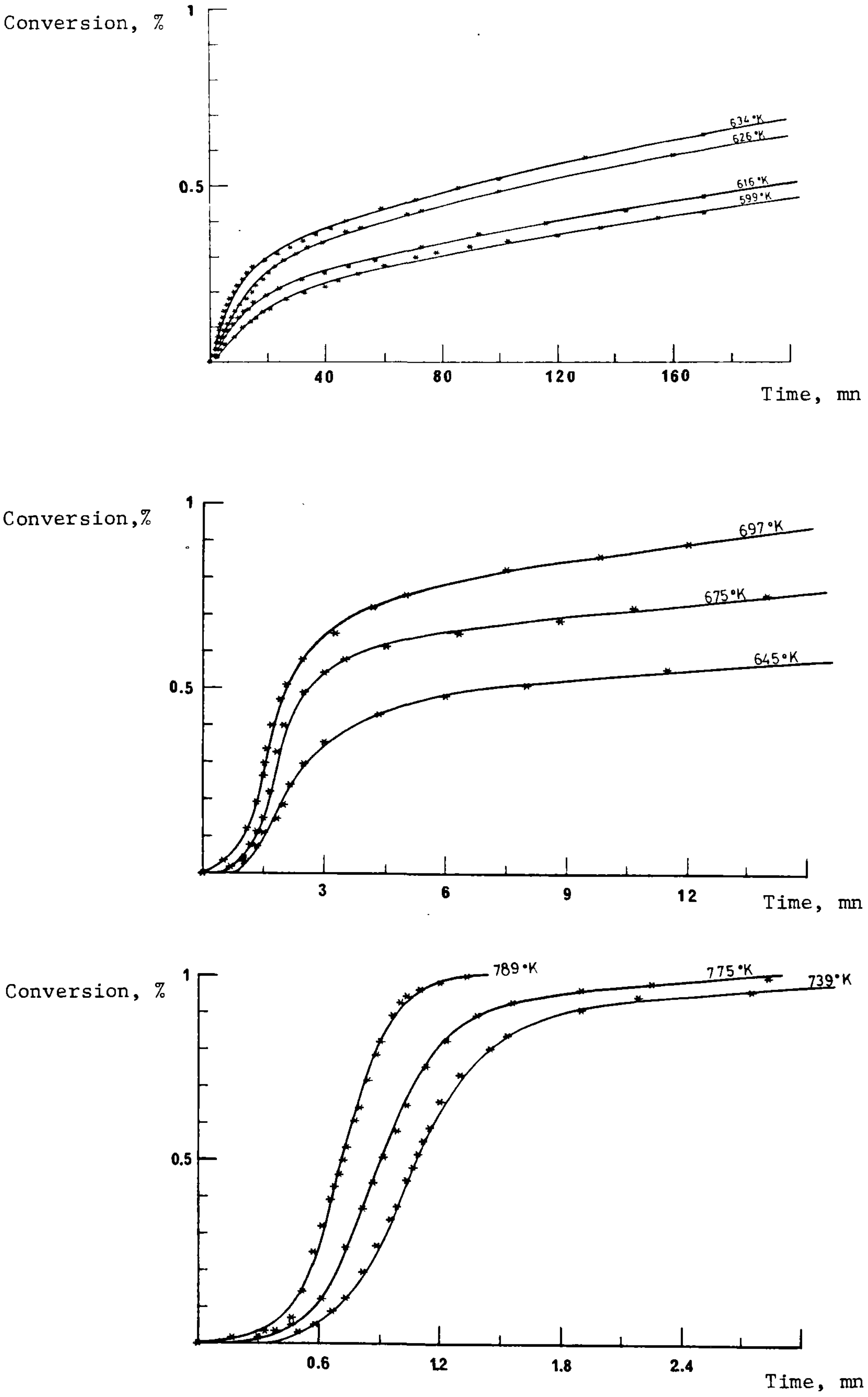


Figure 7 - Pyrolysis curves of tyre sample versus temperature.(9)

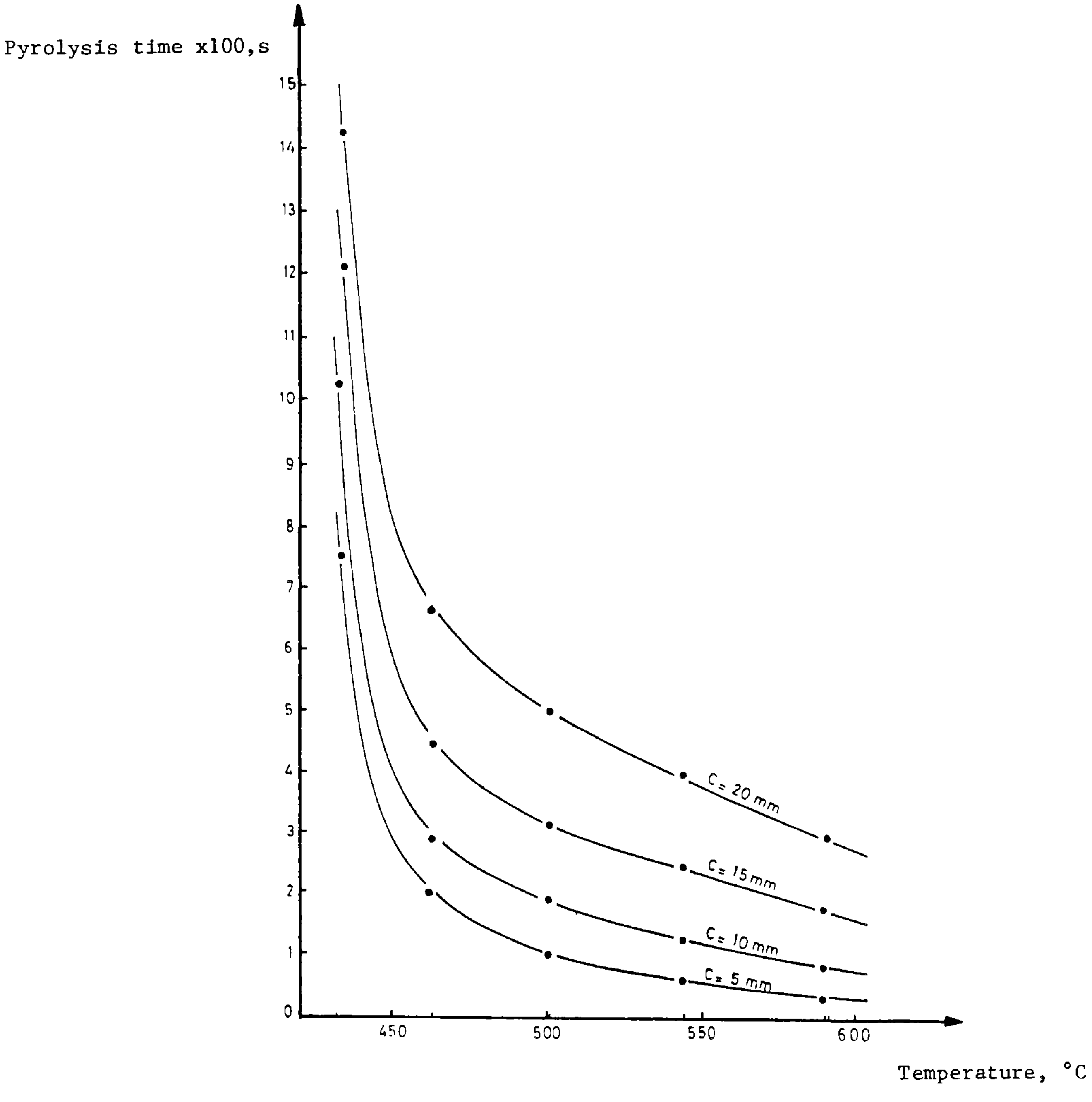


Figure 8 - Effect of temperature and sample size on pyrolysis time.(9)

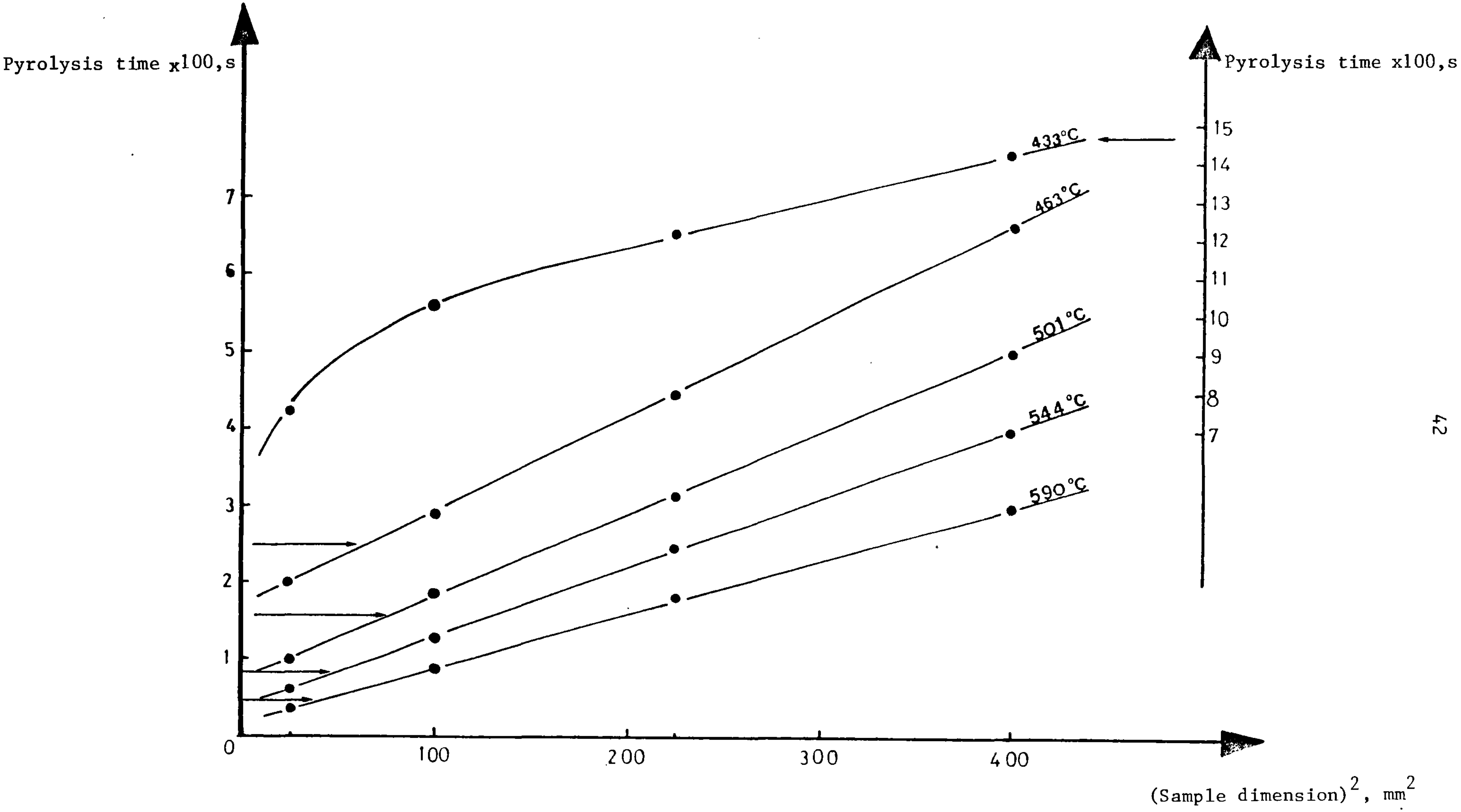
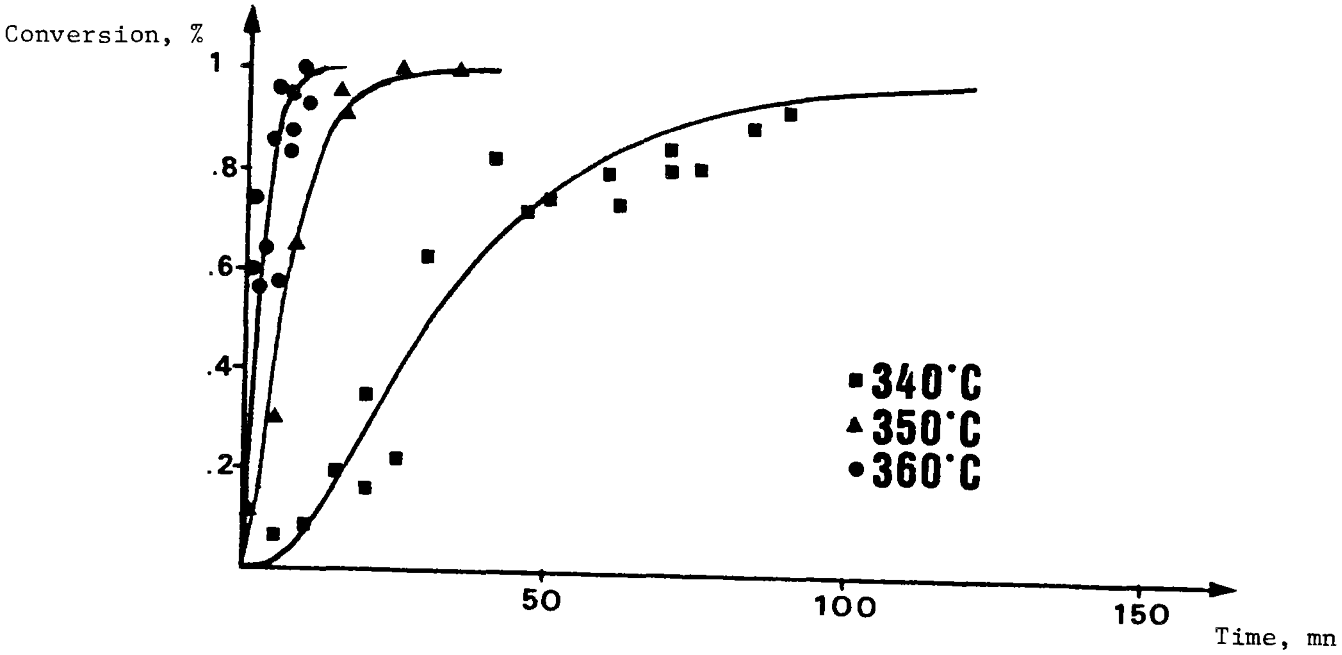


Figure 9 - Evolution of pyrolysis time versus sample geometry at different temperatures.(9)



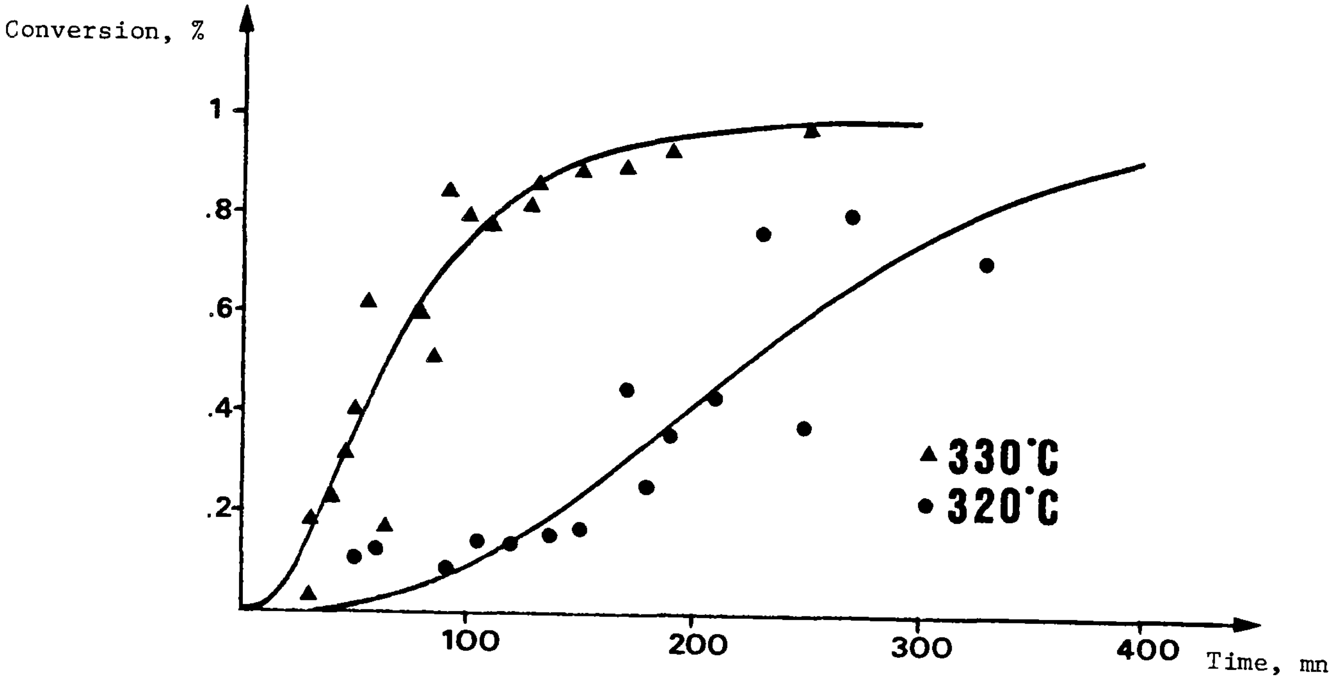


Figure 10 - Curves of pyrolysis in solvent liquid medium versus temperature.(11)

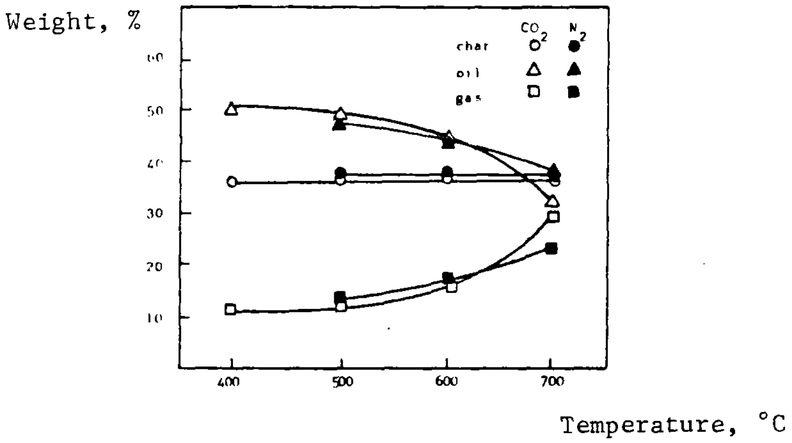


Figure 11 - Product yield versus pyrolysis temperature and nature of vector gas (N_2, CO_2).(19)

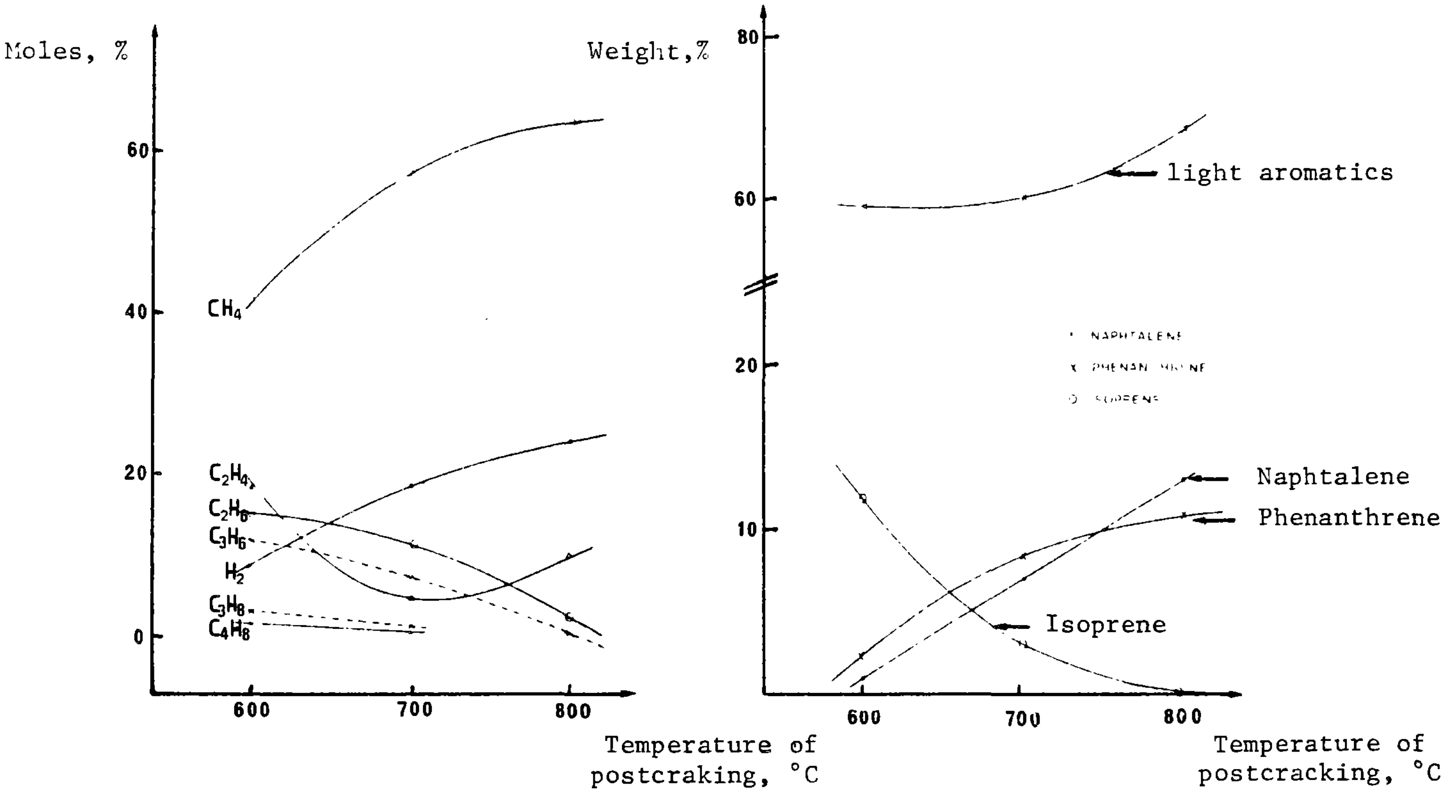


Figure 12 - Gazeous and liquid components from tyre pyrolysis. (17)

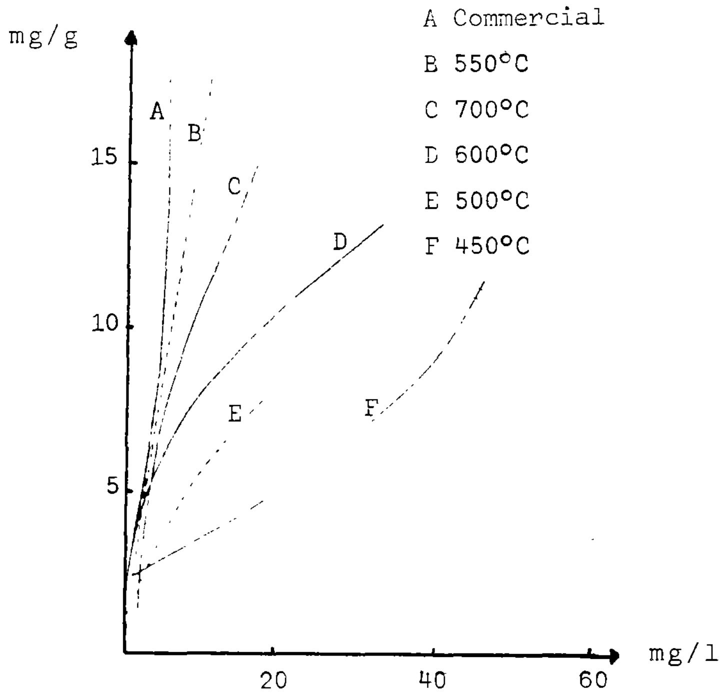


Figure 14 - Adsorption isotherms of phenol on pyrolysis and commercial activated carbon (17).

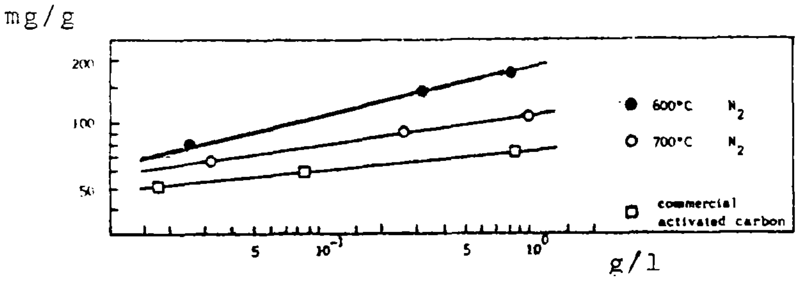


Figure 13 - Adsorption isotherm of orange II on pyrolysis and commercial activated carbon (19).

II. THE PYROLYSIS PROCESSES

The aim of a lot of works about the rubbers and tyres pyrolysis has been the conceiving of industrial processes. So, these processes are numerous and differ in :

- the type of reactor,
- the heat transfer means,
- the operating conditions,
- the size ot the incoming materials,
- the running (continuous or batch).

1. GENERAL DESCRIPTION OF PROCESSES.

The main and common characteristics of pyrolysis processes can be described.

In a first stape, the tyres waste are shredded until 2 - 15 cm sizing. Some processes are able to be fed by whole tyres : itis an appreciable progress and a financial advantage. The incoming of the waste is operated into a reactor. 5 types can be distinguished :

- fluidized bed,
- rotary kiln,
- screw conveyor biler,
- fixed counter flow bed,
- retort reactor.

Figure 15 shows a schematic diagram of a fluidized bed pyrolysis reactor. The too principal advantages of a fluidized bed are the good solids mixing and uniform solids temperature in the fluidized bed. The most important disadvantages of a fluidized bed are the need to remove entrained solids from the vapours and the need to provide fluidizing gas. The vapors leave the vessel with the fluidizing gas and entrained small clear particles, which are usually removed in a centrifugal separator and returned to the bed.

The rotary kiln pyrolysis reactor is shown on figure 16. Here, solids travel through a rotary kiln in plug flow. The usual practice with a rotary kiln is to place paddles on the inside wall of the kiln to continuously lift solid material away from the bottom, then drop it so it falls through the gases in the kiln ; this solid gas contacting pattern gives good temperature uniformity at any position along the length of the reactor. The primary difficulty with this type of reactor is the large area that needs to be sealed, which makes excluding air difficult.

The screw conveyor kiln pyrolysis reactor is shown in figure 17. This reactor design has in common with the precedent the plug flow of solids are moving by a screw inside the kiln. Generally, heat transfer is by contact with reactor wall. This reactor design is easier to seal than the rotary kiln, and it is mechanically simpler.

The fixed counterflow bed pyrolysis reactor (figure 18) is very simple. Rubber pieces are falling down while contacting gas are going up as a counterflow contact. Contacting gas is whether nitrogen or incondensable pyrolytic gas.

The retort pyrolysis reactor is more adapted to whole tyre pyrolysis. After the reactor is cooled, tyre pieces or whole tyres can be loaded through the open door, the door can be closed, air can be purged from the reactor, and heat can be applied. Pyrolysis time depends on the operating conditions. At the end of the cycle, the reactor door is opened, the solids are removed, and the reactor is loaded for a new cycle. Simplicity and ease of sealing are the greatest advantages, but productivity are relatively low. Heat can be applied to exterior surface by circulating combustion gas (figure 19a).Heat can be also realized by direct contact with gas or liquid (figure 19b).

Other reactor types, such as molten salt, plasma, and microwave, have been studied in experimental facilities, but none has been commercially operated.

The solids leaving the pyrolysis reactor are cooled in the solids recovery system. Partial size reduction to break up large agglomerates allows steel removal by magnetic separation. The remaining material is char. If the pyrolysis is made by solid liquid contact, steel is removed by simple filtration and char is suspending in the liquid.

The vapours released by pyrolysis are typically cooled in a quench tower, which can be operated to collect either all of the pyrolytic oil or the high-boiling pyrolytic oil fraction. The gas remaining after pyrolytic oil recovery is typically composed of paraffins and olefins with carbon numbery up to five.

Recently, Idaho National Engineering Laboratory, under U.S. Department of Energy Contract, has published a report on a technical and economical evaluation of scrap tyre pyrolysis (36). The pyrolysis technology assessment identified 31 existing facilities. These facilities use a wide variety of processes, with a number of reactor types, process conditions, and heat transfer media. Only about half of the projects are still active. The others have been abandoned, typically for economic reasons (table 19). Examination of this table leads to several general observations :

- Many projects have been abandoned, either for technical reasons or for economic reasons. Some projects are active but supported by the authorities for environmental reasons (Wobe Steel process for example). Others projects are in the planning, construction, or commercial operation stage.
- All but seven processes require some form of tyre feed preparation, such as shredding, grinding, ...

- Process throughputs vary from the bench scale experiments rated at a few pounds per hour of tyre rubber to designs for commercial plants rated at 1110 000 TPY.
- In most of the processes, rubber is continuously fed to the reactor.
- The division between processes using extermal or internal heat addition to the reactor is essentially even.
- The most common process heat source is recycled product gas, which is used to fire heating tubes or the heat secondary heat transfer media such as molten salt, ceramic balls, steam, or hydrogen.
- Reactor types includes retorts, rotary kilns, fluidized beds, conveyor kilns, hot oil baths, molten salt baths, arc plasma, and microwave ranges.
- Reaction temperatures range from 460 to 1 830 OF.

Although some would not consider the oxidative processes as true pyrolysis processes, they have been included for reasons of comparison with the reductive processes.

The net energy balances for some of the projects where the information is a ailable suggest that the energy recovery is about 75 to 82 % based on the heat of combustion of the tyre rubber. The energy requirement for some of the tyre shredding processes varies from 1.5 to 6 % of the net energy recovered in the products.

Because of technical and economical limitations of most processes, we have selected four of them which chances of development are greatest : Tyrolysis process, DRP-Hambourg University Process, Technology University of Compiegne - IFP Process, Kutrieb process.

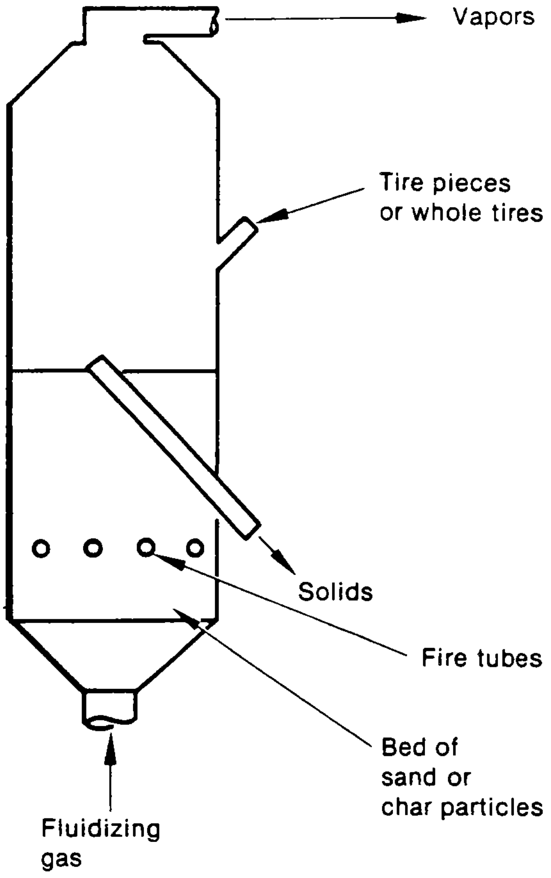


Figure 15- Fluidized bed pyrolysis reactor (36)

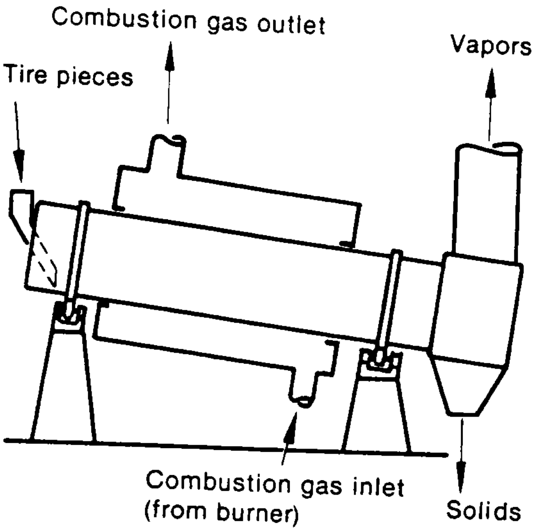


Figure 16 - Rotary kiln pyrolysis reactor (36)

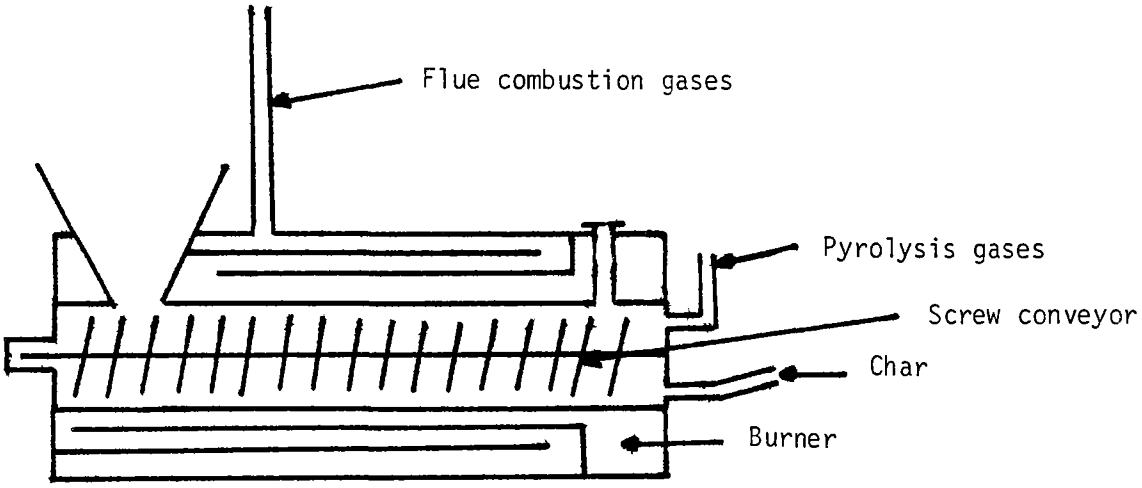


Figure 17 - Screw conveyor kiln pyrolysis reactor

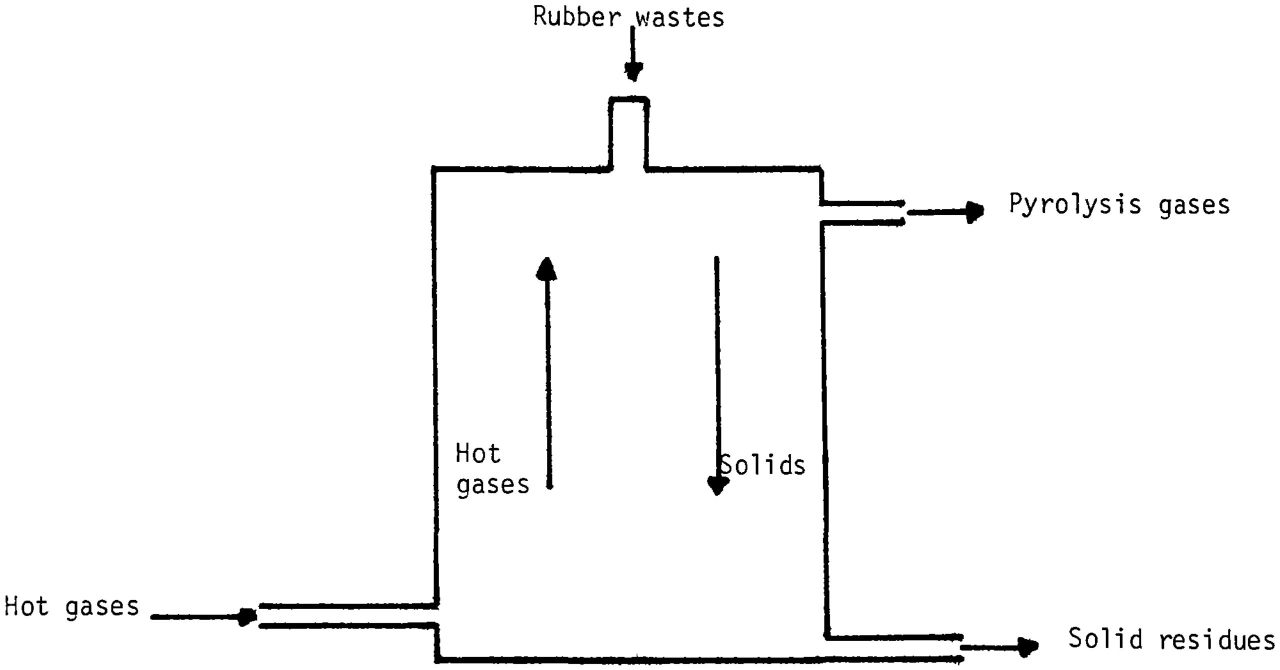


Figure 18- Fixed counterflow bed pyrolysis reactor

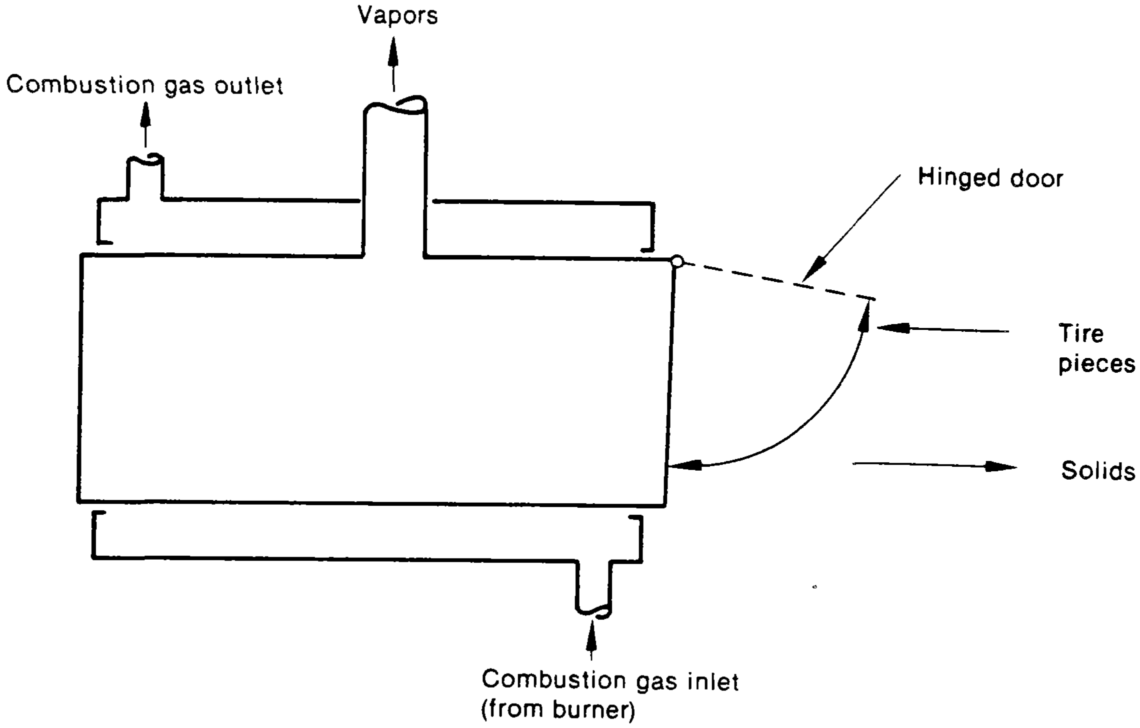


Figure 19a - Retort pyrolysis reactor ; indirect heat transfer (36)

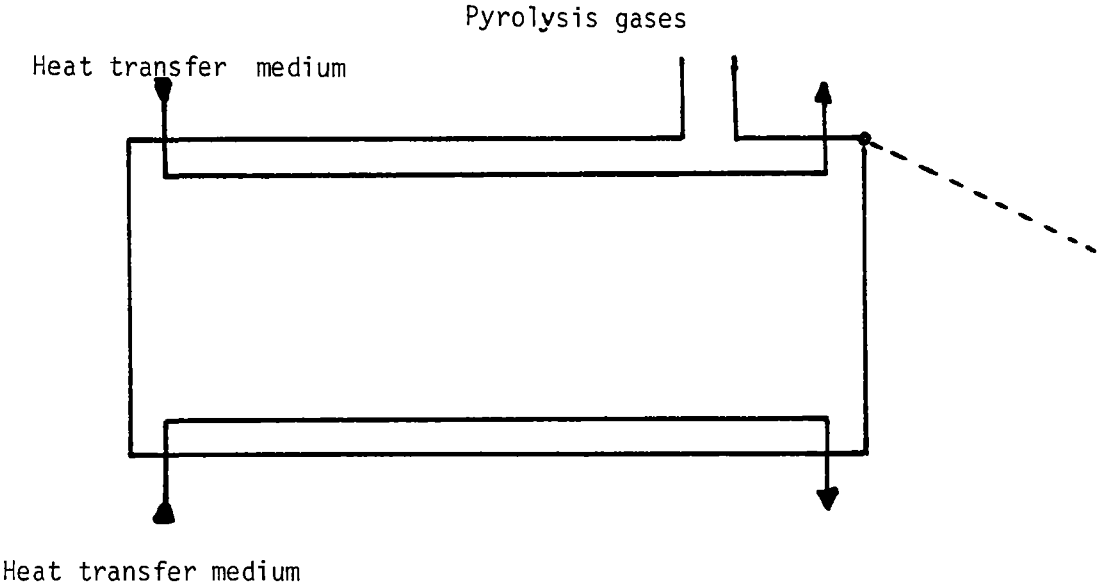


Figure 19b - Retort pyrolysis reactor ; direct heat transfer

	Name	Status (January 1983)	Tire Preparation	Operation[a]	capacity (TPD)	reaction temperature (OF)	Heat Transfer Medium	Heat Source	Reactor Type
OXIDATIVE									
1	Quinlynn	Construction design	Shredded	C	120	1100	Gas	Oxygen	Vertical retort substoichiom'
2	Atomic International	Abandoned	Shredded	C	<0.1	1690	Molten salt	Air	Marshall furnace substoichiometric
3	Nippon Zeon	Abandoned	Shredded	C	26.5	840 to 930	Gas	Tire fragments	Fluid bed substoichiometric
4	Sumitomo	Abandoned	Whole	B	5	1300	Steam	High frequency	Retort
5	Tosco	Abandoned design	Shredded	C	15	900 to 1000	Steam & ceramic balls	Recycled gas	Rotary kiln
REDUCTIVE					300				
6	Kobe steel	Commercial	Shredded	C	26.5	930	Kiln wall	Recycled gas & oil	Rotary kiln
7	MVU	Planned	Shredded	C	2.6	1200 to 1300	Kiln wall	Recycled gas	Rotary kiln
8	Herko Kiener	Construction	Shredded	C	238[a]	1020 to 1110	Kiln wall	Recycled gas	Rotary kiln
9	BKM	Construction	Shredded	C	158[a]	N/A	Kiln wall	Recycled gas	Rotary kiln
10	ERRG	Pilot plant construction	Shredded	C	3 25	1600	Kiln wall	Recycled gas	Paddle conveyor
11	Carbon oil & gas	Commercial	Shredded	C	60	1100	Reactor wall	Recycled gas	Belt conveyor
12	Intenco	Planned	Shredded	C	100	900 to 950	Molten salt	Molten salt	Screw conveyor
13	Nippon Oils & Fats	Abandoned	Shredded	C	26.5	930	Reactor wall	Recycled gas	Screw conveyor
14	Kutrieb	Commercial	Whole	B	6[a]	800	Reactor wall	Recycled gas	Retort
15	Garb-Oil	Planned	Shredded	SC	112.5	1700 to 2000	Fired tubes	Recycled gas	Retort
16	Yokohama	Abandoned	Shredded	B	2.2	930	Recycled gas	Recycled gas & oil	Retort
17	Onahama	Commercial	Shredded	C	30	750	Recycled gas	Recycled gas & char	Retort
18	Firestone	Abandoned Abandoned Abandoned	Shredded Shredded Shredded	B B C	0.2 0.2 N/A	930 1650 1650	Reactor wall Reactor wall Reactor wall	Electricity Electricity Electricity	Retort Retort Retort
19	Oil-Tec	Abandoned	Shredded	N/A	15	N/A	Reactor wall	Tire fragments	Retort
20	Bergbauforschung	Abandoned	Whole	B	1.3[a]	1470 to 1830	Reactor wall	N/A	Retort
21	DRP	Construction	Whole	C	25	1330	Gas	Recycled gas	Fluidized bed
22	Kansas State	N/A	Shredded	C	0.3[a]	1155 to 1450	Gas & steam	Propane	Fluidized bed
23	Occidental	Abandoned	Shredded (24 mesh)	C	300	1000	Nitrogen	Recycled gas	Entrained bed
24	Tyrolysis	Construction	Shredded	C	165	840 to 1110	Gas	Recycled gas	Counterflow gas
25	Uniroyal	Abandoned	Shredded	C	N/A	N/A	Gas	Recycled gas	Crossflow gas
26	HRI	Abandoned	Shredded	C	1000	850	Hydrogen	Recycled gas	Ebullated bed - hydrogenat catalyst
27	Institut Français	Pilot plant design	Whole	B	0.75	700	Oil	Electricity	Hot oil depolymerization
28	University Aston	Abandoned	Whole	B	33	N/A	Molten salt	N/A	Molten Salt
29	Plasma	Abandoned	Whole	B	120[a]	N/A	Arc plasma	Electricity	Arc plasma
30	Osaka	Abandoned	Shredded	B	<0.1	N/A	Microwave	Electricity	Microwave
31	USSR	N/A	N/A	B	<0.1	N/A	N/A	N/A	N/A

[a] B Batch, C - Continuous, SC Semicontinuous, N/A Not applicable

Table 19 - Tyre pyrolysis projects (ref. 36)

2. PROCESSES DESCRIPTION.

2.1. Tyrolysis Process. Foster wheeler Power Products Ltd.

2.1.1. Principle. General presentation of development steps (28-30).

Tyrolysis Ltd is a company which has been formed to own and operate tyre pyrolysis plants in the United Kingdom. Tyre pyrolysis is a process for converting used automative tyres into a light fuel oil, a good solid fuel and a high grade steel scraps.

The tyrolysis Technology was purchased by Foster Wheeler Power Products Ltd. from Batchelor Robinson Metals and Chemicals Ltd. in February 1981 to complement that which they already prossessed in other fields of pyrolysis. Foster wheeler became involved in the pyrolysis of a variety of waste materials in the mid 1970, when they agreed to cooperate with Warren Spring Laboratory in the development of the Cross Flow System. This process, which was aimed primarily at domestic refuse, was the out come of work undertaken by Warren Spring under instructions from the Department of Industry and patent cover was subsequently obtained by the National Research and Development Corporation. Foster wheeler now hold a world wide licence for the cross flow system but the decision to purchase the Typolysis technlogy was taken because of the emphasis Batchelor Robinson had placed on developing a process to handle one specific type of waste material, tyres, the attention they had devoted to solving the mechanical handling problems posed by the unique physical properties of tyres, and the scale at which they had been working.

The tyrolysis development stemmed from work which Batchelor Robinson did in 1974 into the possibility of a recovery operation based upon scrap tyres. After a search of the then available technology and an intestigation of scrap tyre arisings a pyrolytic technique was chosen as that most likely to provide a commercially viable operation. In early 1975 Warren Spring Laboratory were therefore Commissioned to design, build and operate a tyre pyrolysis plant on behalf of Batchelor Robinson.

This plant was in intermittent operation until 1978 at a scale of up to 1 800 tonnes per year and was followed by a programme of laboratory work and full scale testing of key mechanical handling aspects. The latter included comprehensive trials on the shredding of tyres, the extraction of solids from the reactor and reactor sealing systems with the results from this whole development programme, including that undertaken directly by Foster Wheeler, being brought forward to provide the basis of the design for the commercial plant.

2.1.2. Process description (30).

The first commercial plant is located in Wolverhampton (U.K.) for obtaining scrap tyres as this area is the heart of the tyre industry. Its capacity is 50 000 metric tons in a 7 200 hours year. The construction is finished few months ago and the unit is probably just operating now.

Figure 20 is a simplified process flow diagram. The three main sections are :

Feed storage and loading.

Tyres of any size up to 1.75 metres diameter are ded via front end loaders and a fixed crane into a double rotor knife mill. This shreds the tyres and any associated foreign matter with the product being sized in a rotary screen to give a nominal 100 mm maximum size. Output is then weighed in a hopper and conveyed to the top of the reactor in 240 kgm batches for feeding into the reactor lock hoppers. Oversize shred from the screen is re-cycled back to the knife mill for further size reduction and a buffer stock equivalent to approximately four days plant throughput will be held to alleviate any maintenance difficulties.

Reactor, oil and gas process loops.

Shredded tyres enter the reactor through a purged triple valve, double chamber sealing system. Hot oxygen free gases pass through the bed of tyres in the base of the reactor in a counter-current fashion causing pyrolysis to occur. The operational temperature range is 450° C - 550° C and the reactor gas velocity range is 0.3-1 m/s ; residence time of gases in the

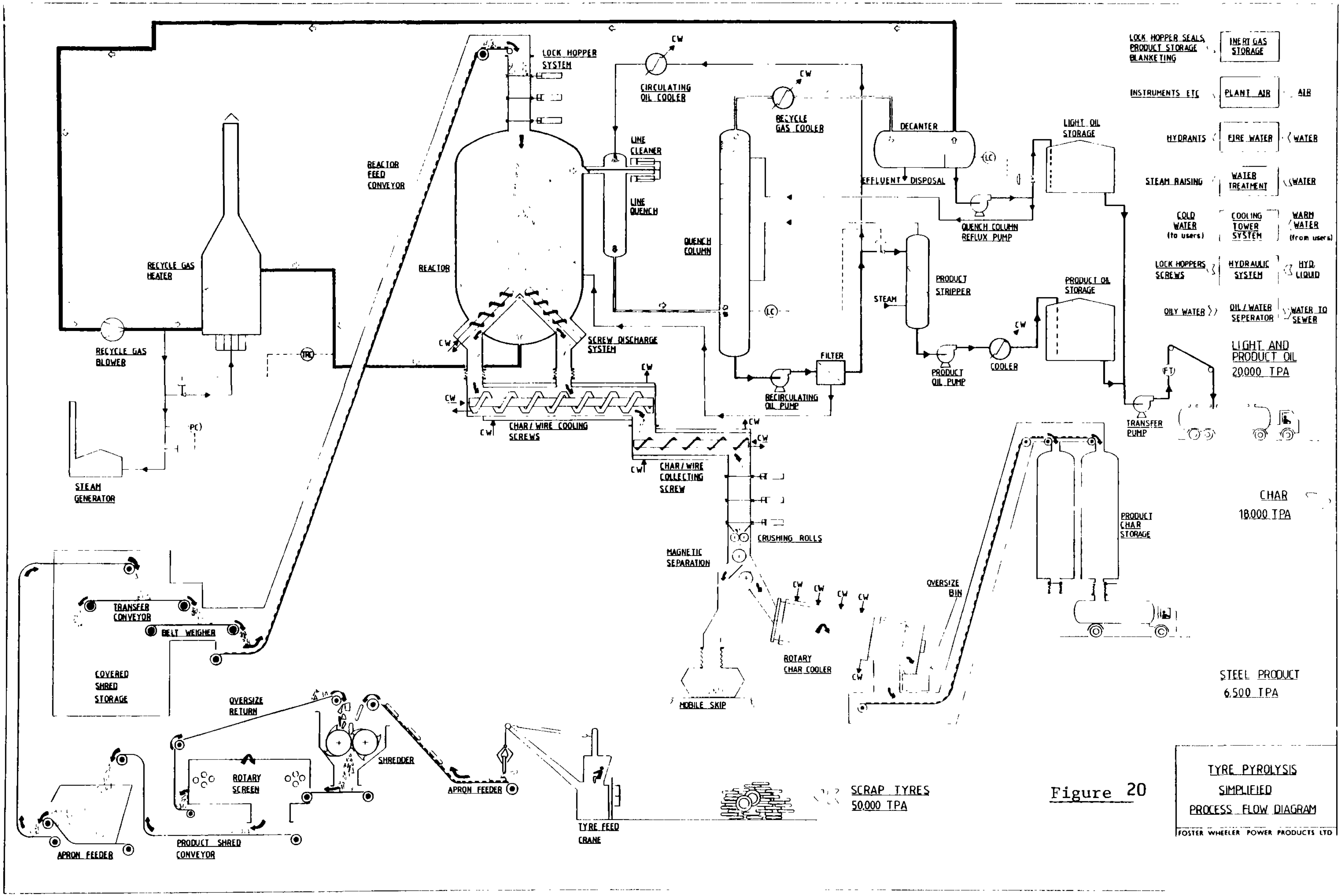

LOCK HOPPER SYSTEM
CW
CIRCULATING OIL COOLER
CW
RECYCLE GAS COOLER
DECANTER
LINE CLEANER
LINE QUENCH
REACTOR FEED CONVEYOR
REACTOR
QUENCH COLUMN
EFFLUENT DISPOSAL
(LC)
LIGHT OIL STORAGE
QUENCH COLUMN REFLUX PUMP
RECYCLE GAS HEATER
RECYCLE GAS BLOWER
TRC
PC
STEAM GENERATOR
CW
SCREW DISCHARGE SYSTEM
CW
CW
CHAR / WIRE COOLING SCREWS
CW
CW
CW
CHAR / WIRE COLLECTING SCREW
CRUSHING ROLLS
MAGNETIC SEPARATION
CW
CW
CW
CW
ROTARY CHAR COOLER
MOBILE SKIP
CW
OVERSIZE BIN
(LC)
FILTER
RECIRCULATING OIL PUMP
STEAM
PRODUCT STRIPPER
PRODUCT OIL PUMP
CW
COOLER
PRODUCT OIL STORAGE
(FT)
TRANSFER PUMP
PRODUCT CHAR STORAGE
LOCK HOPPER SEALS, PRODUCT STORAGE BLANKETING
INERT GAS STORAGE
INSTRUMENTS ETC
PLANT AIR
AIR
HYDRANTS
FIRE WATER
WATER
STEAM RAISING
WATER TREATMENT
WATER
COLD WATER (to users)
COOLING TOWER SYSTEM
WARM WATER (from users)
LOCK HOPPERS SCREWS
HYDRAULIC SYSTEM
HYD. LIQUID
OILY WATER
OIL / WATER SEPERATOR
WATER TO SEWER
LIGHT AND PRODUCT OIL 20,000 TPA
CHAR 18,000 TPA
STEEL PRODUCT 6,500 TPA
TRANSFER CONVEYOR
BELT WEIGHER
COVERED SHRED STORAGE
OVERSIZE RETURN
ROTARY SCREEN
SHREDDER
APRON FEEDER
TYRE FEED CRANE
SCRAP TYRES 50,000 TPA
APRON FEEDER
PRODUCT SHRED CONVEYOR
TYRE PYROLYSIS SIMPLIFIED PROCESS FLOW DIAGRAM
FOSTER WHEELER POWER PRODUCTS LTD

Figure 20

reactor is comprise between 2 to 6 seconds. These hot gases, now supplemented by pyrolysis product gas and oil in the vapour phase, leave the reactor through a short overhead line and enter the line quench where they meet a spray of cold product oil. This causes the product oil in the vapour phase to condense and all the oil then collects in the base of the primary quench tower. Oil is drawn from this tower on a level control, filtered, and the net make is fed into a stream stripper where the flash point is adusted before further filtering, cooling and pumping to product storage. The remainder of the oil is circulated through an exhanger to lower its temperature and back into the line quench.

An alternative partial quench mode is available to provide a degree of fractionation to product oil by side drawing lighter fractions in the column.

Gases come overhead from the quench tower at a temperature in the region of 90° C and contain light condensibles and water in the vapour phase.These are condensed in the overhead condenser where the temperature is dropped to around 30° C, and collect in the decanter where the lights and water are separated. The light fraction from the decanter is taken to either provide reflux on the quench tower or pumped to product storage while the water passes, via an effluent stripper, to drain.

Clean gases from the decanter pass through a knockout drum into the re-cycle blower. From this blower they are either bled to flare or used as the priority fuel for the fired heater, or pass through the tubes of the heater where their temperature is raised, and back into the reactor. Bleed to either flare or fuel gas is controlled by a pressure controller on the knockout drum which is maintained at a pressure slightly above atmospheric.

Solids, consisting of a friable carbonaceous char and lengths of steel wire, are removed from the reactor bed by large inclined screws. From these they fall under gravity into hollow flight screws where they are indirectly cooled to a temperature below the ignition point of the char. They are then collected in a final screw conveyor which feeds them into a purge triple valve, double chamber lock hopper system, from which they leave the reactor atmosphere.

Solid product handling and storage.

Solids leaving the reactor atmosphere fall into counter-balanced rolls which provide a controlled feed to a double drum magnetic separation system. This separates the steel from the char, with the steel passing directly to a baling press while the char enters a pneumatic conveying system using steam as the conveying medium. After classification to eliminate any non-magnetic foreign matter the char is cooled further within the conveying system by water being sprayed in such a fashion as to avoid the temperature in the system falling below the dew point. Char is removed from the steam stream by a cyclone and bag filters, cooled further in a small jacketed screw conveyor to large elevated silos by bucket conveyors.

2.1.3. Products characteristics (30)

Product yield are typically following :
40 % weight to liquid hydrocarbons
35 % to carbonaceous solids
15 % to steel
10 % gas.

The composition of recycle gas is given in table 20 ; we note important quantities of olefins, which it is logical as discussed in chapter I. The presence of water, oxygen, carbon monoxide, carbon dioxide are normal because a part of gas is from combustion gas.

Components	Composition, % Wt
H_2O	2.22
N_2	2.81
O_2	0.45
H_2	1.14
CO	11.46
CO_2	9.51
CH_4	29.05
C_2H_6	6.58
C_2H_4	12.69
C_3H_8	1.51
C_3H_6	5.51
C_4H_{10}	3.92
C_4H_8	1.54
C_4H_6	1.58
C_6H_{14}	9.14
H_2S	0.75

Table 20. Recycle gas analysis properties.

Properties of tyrolysis oil are as per table 21. Authors intend to fractionate oil from industrial unit so as to determine the composition.

Properties	Test method	Tyrolysis oil
Flash point, ° C	ASTM D.93	> 65
Viscosity at 180° F, Cst	ASTM 445	< 11.8
Ash, % Wt	ASTM D482	< 0.1
Water, % vol.	ASTM D95	< 0.5
Sulphur, % Wt	ASTM DI551	1.2
Pour point, ° C	ASTM D97	-9
Asphaltenes, % Wt	IP 143	< 0.5
Sediment, % Wt	ASTM 0473	< 0.1

Table 21. Properties of Tyrolysis oil.

The composition of char is presented in in table 22 and its calorific value is comprised between 6 000 to 7 500 kcal/kg.

Composition	Specification
Moisture, % Wt	10
Volatiles, % Wt	5-10
Ash, % Wt	20
Sulphur, % Wt	3
Typical elemental analysis	
Carbon, % Wt	79.85
Hydrogen, % Wt	0.95
Sulphur, % Wt	2.97
Zinc, % Wt	4.95

Table 22. Char properties.

Finally, the steel has properties shown in table 2.3.

Elements	Specification
Tin, % Wt	0.02
Copper, % Wt	0.24
Sulphur, % Wt	0.35
Phosphorus, % Wt	0.03
Carbon, % Wt	4.0
Chromium, % Wt	0.05
Molybdenum, % Wt	0.01
Nickel, % Wt	0.05
Manganese, % Wt	0.70
Silicon, % Wt	0.5

Table 23. Steel waste properties.

Significant samples of oil and char have already been subject to test burns and no problems are foreseen in using these as fuels for utility or industrial use. Also, the process uses its own fuel (gas).

2.1.4. Technical and economical discussion (30, 31).

For a 50 000 t/y Tyrolysis plant, yields are :
20 000 t/y fuel oil
18 000 t/y solid fuel
6 500 t/y steel scrap.

Gas is consumed in the plant. From informations obtained electric power consumed and gas required are respectively 1 500 kw per ton, i.e. 3.52 GJ/t. Taken into account the calorific value of fuel oil, carbonaceous residue and gas, which is approximately 3.18 GJ/t, i.e. energy yield 89 % compared to calorific value of products.

The major assumptions are that the project will have a 10 years operational life and capital cost, excluding land, is estimated at U.S. dollars 15 millions, which is very high.

The key areas of work where there exists scope to entrance profitability concern merely :

Capital cost reduction.

Initial processing facilities are specified so a conservative design to ensure high reliability. It should be possible to undertake a value engineering exercise on the design once detailed operational experience is assessed.

Product refinment.

Char to low grade carbon black (mats, boots, ...).
Char to active carbon.
Fractionation of product oil to valorize some particular fractions.

Difficulty is to translate these projects into commercial practice so as the market assessments justify adequate pay back.

At present, the sure use of products is just an energy valorization and it is probably not sufficient to cover capital and operational costs.

2.2. D.R.P. - Hamburg University Process.

2.2.1. Principle - General presentation of development steps (18, 22).

D.R.P. GmbM and the University of Hamburg propose a solution to overcome the recycling problems of scrap tyres and plastic waste by employing a fluidized bed pyrolysis process. This continuous process transforms these materials into organic chemical raw materials without hardly any residues.

The University of Hamburg has been developing a fluidized bed process for the pyrolysis of plastic waste, scrap tyres and lately Biomass since 1970. They used three stages of up-scaling : 0.1 kg/h ; 10 kg/h ; 100 kg/h. The research aim is, on the one hand, the optimal disposal of the wastes but also the recovery of worthwhile materials from these compounds, which contain a high proportion of hydrocarbons.

General principle of this pyrolysis process is following ; the reactor, a fuildized bed, is located in a heat - insulated reactor, heated either by electricity or by burners to between 600 and 900° C. The scrap tyres fall either through a lock into the reactor or are carried by a screw conveyor into the fluidizing bed. Fluidized bed has particular advantages : no mechanical moving parts in the hot areas, an homogeneous temperature field, an homogeneous product spectrum, a completely closed system, an easy moving of solids out of the reactor zone and separation by a cyclone.

The pyrolysis products leave the reactor, solids and carbon balck being separated out. The cleaned gases pass through a cooler, in which the liquid hydrocarbons condense, subsequently being split in a distillation column and collected as worthwhile products. The non condensable gases are compressed and used as the fluidizing medium and as the burner gas.

For the laboratory experiments, an apparatus made of quartz and developed by MENZEL (32) with a fluidized bed diameter of 5 cm, was used. It was possible to achieve a continuous feed of about 100 g/h of granulated rubber from scrap tyres. These experiments led to the planning, building and operation of a pilot plant.

The pilot plant, with a minimum throughput of 10 kg/h, involved a factor increase of 100 over the laboratory plant. To avoid any pollution of the products, gas heated radiating firetubes were used. This plant has been in operation for more than 700 h, during which more than 5.000 kg of plastic and rubber waste have been pyrolyzed. It was proved through these experiments that the non-condensable gas is more than enough to supply the heating requirements of the process. The firetubes permitted temperatures of up to 850° C to be maintained in the fluidized bed.

The feed enters the sand bed either at the top of the reactor through an air lock or through a water cooled screw feeder at the side. The reactor is built up with three parts, each of a diameter of 0.5 m and different lenths of 1 m , 0.5 m and 0.3 m. The power output of the four burners is regulated by varying the pressure of the burning gas.

2.2.2. Process description (23).

Since the fluidizing bed showed itself surprisingly insensitive to the size of the feed material - pieces of tire of up to 2.7 kg in weight could be pyrolyzed by the pilot plant - the way was open to pyrolyse unshredded tires in a correspondingly large fluidized bed reactor. Thus, as a continuation of the work on pyrolysis carried out at the University of Hamburg, a prototype plant was built to pyrolyze whole car tires, financed by the BMFT* and the Hamburg firm of Carl Robert Eckelmann. Pyrolysis takes place in a firebricklined steel reactor. The actual reaction zone is an area of 900 x 900 mm filled with sand or fine grained carbon black. The fluidizing medium is indirectly heated by 7 radiant fire tubes arranged in 2 layers, up to 650 to 850° C and fluidized by gas blown through it. The gas produced by the pyrolysis of scrap tires is used both for fluidizing and heating the sand bed (figure 21).

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* Federal Ministry for Research and Technology (West Germany)

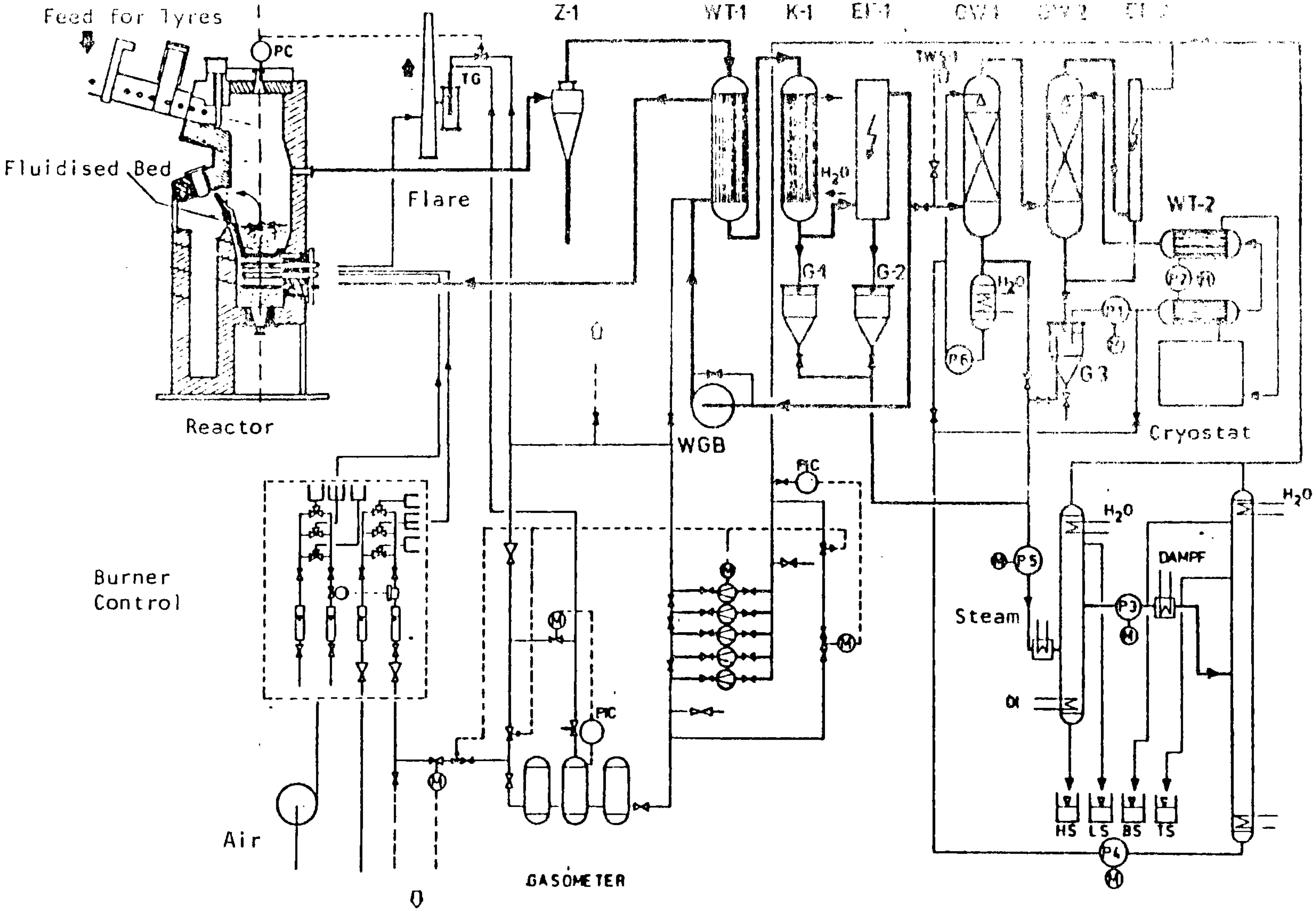


Figure 21- Fluidized bed pyrolysis process flow diagram (23).

The unshredded tires roll through a gas-tight lock and drop into the reactor zone. The maximum throughput of 120 kg scrap tyres per hour, limited by the coupled-on and taken-over parts of the pilot plant, involves the feeding into the reactor of one car tyre approximately every 5 minutes. Heat is transferred to the tyre by the fluidizing sand and at first, only the outer parts break down. Gradually, the complete decomposition into gaseous and solid products such as carbon black, filler materials and steel parts takes place.

The steel wires are taken out of the reactor by a tiltable grate at programmable intervals and deposited in a silo (figure 22). Solid powdery products are carried out of the reactor and separated by a cyclone. The gas then passes through a heat-exchange WT1 and is cooled down to 50° C by a cooler K1. Condensed tars flow into a collecting vessel G1. The gas then passes through an electro-filter EF1 to separate out the remaining carbon black particles and drops of tar.

The gas (about 200 Nm^3/h) is then split into two streams. The main part passes through a vane wheel blower and the heat exchanger WT1 where it is heated up to about 400° C before entering the reactor through the blower tubes which are situated below the radiant fire-tubes. The rest of the gases pass into the processing section of the plant where the liquid pyrolysis products are condensed and distilled.

Water is separated out in water GW1 which is operated by cooled pyrolysis oil ; gaseous and liquid products are separated by the wash-cooler GW2. A prefilled xylene-mixture is used as the washing medium for the washers at the beginning of experiments ; during the pyrolysis this is partially replaced by pyrolysis oil cooled by a cryostat.

Additional condensate formed in the washer GW2 is taken from the collection vessel GW3 and pumped by P5 into the first distillation column. Here the oil is separated into low, middle and high-boiling fractions. The middle-boiling fraction is divided into predominantly benzene, toluene and xylene fractions, the latter being fed back into the washer system. The low-boiling, toluene, benzene and high-boiling fractions are collected and stored in graduated containers.

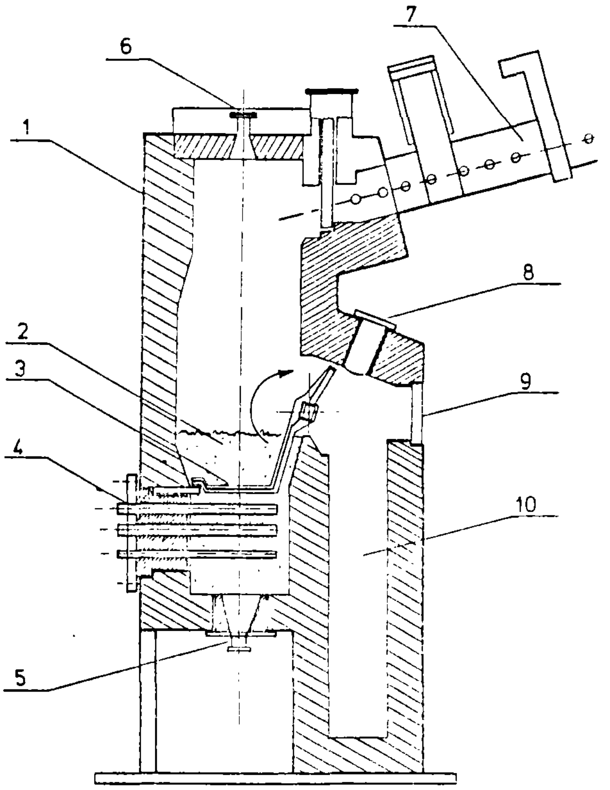


Figure 22 – *Flow diagram of the prototype reactor for whole-tire pyrolysis.*

(1) steel wall with fireproof bricking; (2) fluidized bed; (3) tiltable grate; (4) radiation fire tubes; (5) nozzles to remove sand and metal; (6, 8, and 9) flange for observation and repairs; (7) gastide lock, (10) shaft for steel cord.

Table 24. Composition of pyrolysis products in different scales of fluidized bed reactor.

Reactor	LWS	TWS-1	TWS-2
Feed material	granulated rubber	used places	whole tyres
Temperature ° C	740	750	700
Hydrogen	0.8	1.30	0.42
Methane	10.2	15.13	6.06
Ethane	1.2	2.95	2.34
Ethylene	2.6	3.99	1.65
Propane		0.29	0.43
Propene	0.7	2.50	1.53
Butane		1.31	1.41
Butadiene	0.3	0.92	0.25
Isoprene		0.34	0.35
Cyclopentadiene		0.39	0.25
Other aliphatic compounds		0.36	1.07
Benzene	4.2	4.75	2.42
Toluene	3.8	3.62	2.65
Xylene	1.9	+	+
Styrene	2.3	0.17	0.35
Indan, indene		0.31	0.48
Naphthalene	0.9	0.85	0.42
Methylnaphthalene		0.83	0.67
Diphenyl		0.49	0.39
Fluorene		0.16	+
Phenanthrene		0.29	0.19
Pyrene		0.21	0.06
Other aromatic compounds	17*	8.50	13.67
Carbon monoxide		3.80	1.48
Carbon dioxide		1.95	1.74
Water		0.10	5.11
Hydrogen sulfide	1.9	0.23	0.02
Thiophene		0.15	0.25
Carbon soot, fillers	42.8	40.59	40
Steel cord	7.9	1.62	11.30
Balance	98.5	98.10	96.96

LWS : laboratory scale reactor, TWS-1 : pilot plant, TWS-2 : pilot plant for whole tyres.

* other aromatic and aliphatic compounds

From the washers, the non-condensable components of the pyrolysis gas pass into a tubular electro-filter where finer droplets are collected. The remainder is then compressed by 3 membrane compressors K1-3 and stored in three pressure holders, each with a capacity of 0.5 m^3. Two further compressors K4-5 deliver the gas directly into the fluidizing gas system before the heat-exchanger WT1. Further fluidizing gas for the reactor, burned gas for the seven radiant fire tubes and surphur gas to the flare are all taken from the containers.

2.2.3. Products characteristics (23).

The pilot plant has been running since late 1978. During each run up to 150 whole scrap-tires were pyrolyzed. The balance of the products is as follows :

22 Wt % gas
27 Wt % liquids
39 Wt % carbon black
12 Wt % steel cord.

Table 24 shows a more exact material balance.

A part from the main gaseous products of methane, ethylene, ethane and propene, the liquid products yielded were overwhelmingly aromatics such as benzene, toluene and naphtalene, The sulphur content of the pyrolysis oil is less than 0.4 Wt % and that of the gas less than 0.1 Wt %. The main portion of the sulphur is chemically combined with the carbon black.

2.2.4. Technical and economical discussion (33).

D.R.P. GmbH is now developing an industrial prototype under construction in Bavaria. It is a demonstration plant with a capacity of 8 000 t/year. D.R.P.'s objectives are perfecting the fluidized bed pyrolysis process, marketing ready-to-use pyrolysis plants to eliminate various wastes (plastic waste, scrap tyres in particular), determining the economical feasibility, obtaining large quantities of pyrolysis products to test their qualities.

Two process lines are in building. One of them will be fed with solid material up to 15 cm length of side. The other one will take solid material up to 80 cm length of side, especially whole scrap tyres and pieces of truck tyres.

Efforts to entrance profitability concern principaly the product refinement : optimization of operating conditions, carbon black refinement (mechanical grinding and pelletizing), improve the quality of oil in extracting light aromatics, recycling carbon black in painting industry and low-grade rubber industry.

The capital cost is estimating at U.S. dollars 6 to 7 millions for 8 000 t/y unit.

2.3. Technology University of Compiegne - I.F.P. Process.

2.3.1. Principle - General presentation of development steps (11, 16, 34).

The Technology University of Compiegne and the Oil Research French Institute (I.F.P.) are scaling up a pyrolysis process for recycling tyre rubber and other rubber compounds. The process consists in treating rubber with heavy hydrocarbone which transfer the heat for reaching the required temperature and depolymerisation reactions.

Since 1974, J.M. BOUVIER and M. GELUS (Technology University of Compiegne) have been developing thermal degradation of rubber in solvent medium on a laboratory scale. The chemical basis of the process is very simple. Under an inert or free - oxygen atmosphere in the temperature range of 360° C - 380° C, a piece of rubber is dissolved in few minutes in a heavy oil. Such a solvent is choosen to prevent cracking. It must be able to dissolbe oligomers produced by depolymerization reactions. In this kind of thermal decomposition gas production is very weak, less than 3 % of the polymer waste. Under these conditions, rubber wastes are converted very rapidly in a carbon black-oil suspension. Conversion is as efficient with sulfur vulcanized rubber as peroxide vulcanized one. The suspension can be burnt to produce energy and steam, or, in some specific applications, recycled in a step through the fabrication of rubber goods.

The development work was done during two distinct periods. The first one was completed in 1979, using a medium size plant representative of the solid-oil contact phenomena. The second one started early in 1982 in a large pilot plant suitable for problems of scaling up. Both plants were operated in batch vessels designed for 8 hours of complete operations.
The medium size pilot plant included a batch vessel with a capacity of a few cars tyres and has demonstrated the feasibility of treating whole tyres.

2.3.2. Process description (16).

The large pilot plant built at the end of 1981 is described in figure 23 and comprises the following main parts :

. the whole tyres (100 to 300 kg) are put in a basket (R_1) ;

. the contacting oil representing a total volume of around 600 l per batch ir recirculated in the main loop with the pump P_1 at a flow rate of 30 to 60 m^3/h depending on the viscosity of the bulk liquid ;

. the circulating liquid is heated in the electric heater E_1 up to 380 °C within 3 h ;

. the liquid is sprinkled in the vessel making contact with tyres by trickling and involving much less liquid than with complete immersion ;

. as the different reactions proceed involving thermal cracking of rubber and of the oil the light compounds produced condense in the air exchanger E_3 while the gas goes through the condensing part and is volume metered before exiting ;

. when the depolymerisation reactions are over the bulk liquid phase including the compounds resulting from the tyre degradation is cooled in the air exchanger E_2 down to around 100° C ;

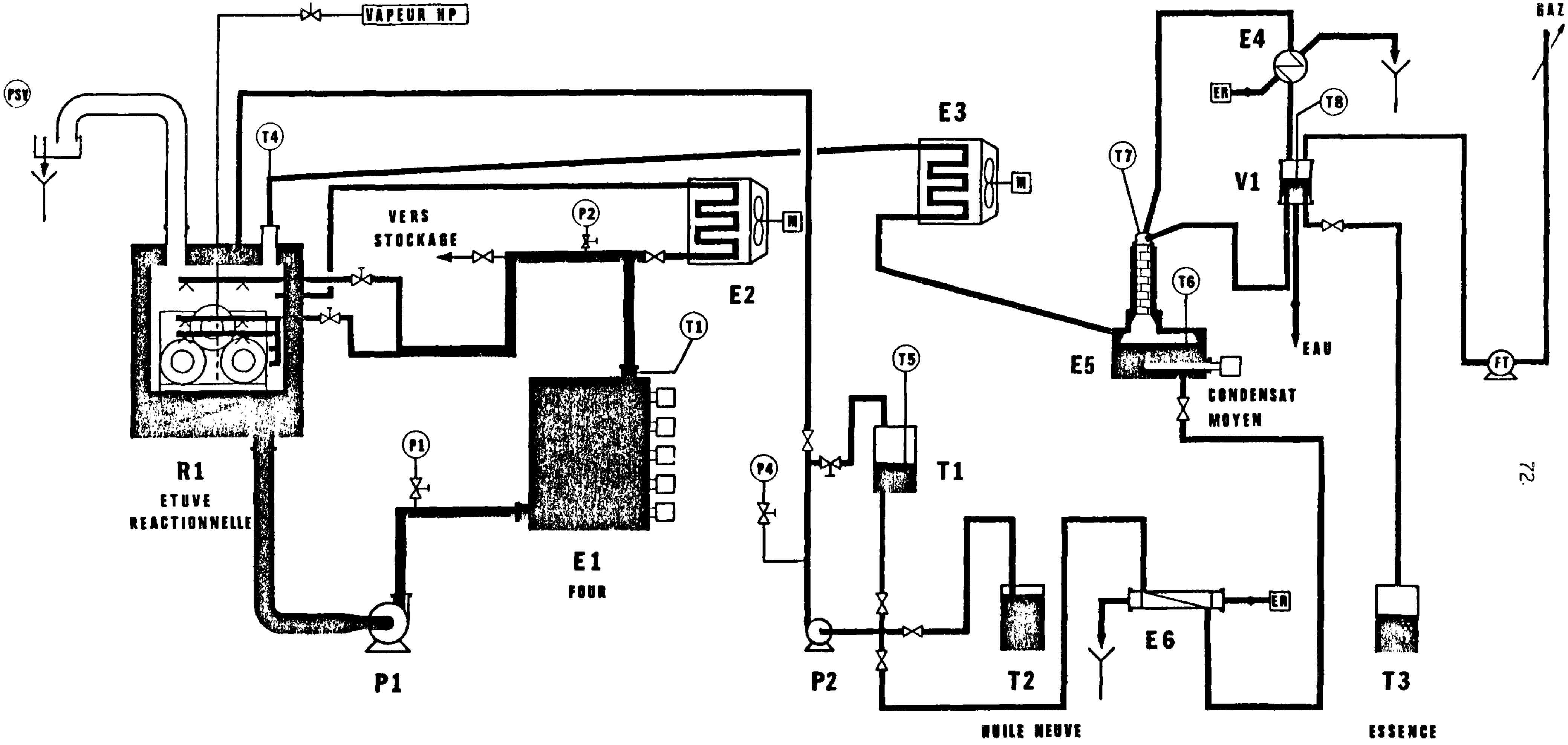


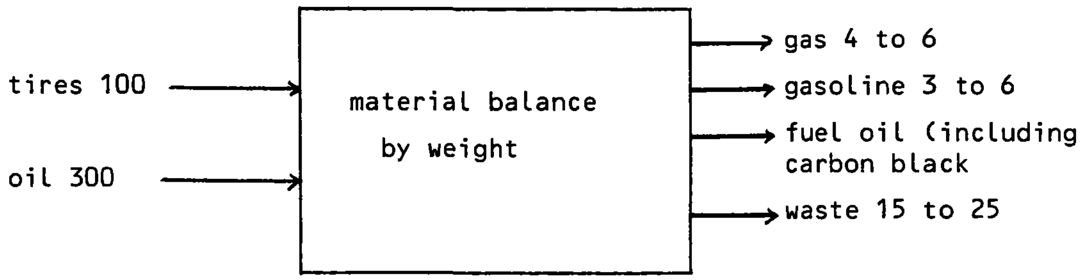
Figure 23- Flow diagram of whole types pyrolysis in solvent medium (16).

- at this stage of advancement of the operation the liquid in the main loop, which is quite comparable to viscous fuel oils is diluted with the light hydrocarbons coming from the bottom of E_5 which favorabbly decrease the viscocity and the pour point of the fuel. The role of E_5 is to remove light gasoline in order to set the flash point of the fuel oil at the specification (> 70° C) and to keep its viscosity in the heavy fuel oil range (110 cSt - 450 cSt at 50° C). If necessary E_5 can supply an additional amount of gasoline to fit the energy requirements of the plant which could be normally provided by a mixed-burner (gas and gasoline).

Material balance.

For each operation the rubber stock is placed in contact with an amount of fresh oil representing about three times the quantity of rubber by weight. When the temperature increases and reaches the range required, the amount of gas and light compounds formed is also dependent on both temperature and residence time. This is the reason why heating is stopped as soon as the rubber has depolymerized when the temperature reaches 370-380° C. Obviously any fresh oil distilling before the required reactor temperature will supply additional condensates.

We describe hereunder a material balance with some data included within a given range because of the differences existing in the type of tires and oils than can be treated. The used oils in these experiments are described later on in this paper.



1 to 3 Wt % of gasoline are removed to get the flash point specification of the fuel oil.

As a first approach the oil can be considered to act as a solvent and heat transferring agent. In an industrial plant the effluents from the reactor would be separated in a column. The amount of gasoline removed from the top can be adjusted so as to supply (with the gas) the energy reguirements of the plant. The top effluents (gas and gasoline) are then separated in a drum. A few quantity of undissolved but depolymerized rubber does stay mixed with the metallic waste depending on the nature of the reactants (aromaticity of the oil and tyres composition).

Problems solved in development.

Reactor : the reactor is made of carbon steel and operated at atmospheric pressure. Because flammable and foul-smelling products are raised to high temperature, it must be tight.

The door of the pilot reactor is a reinforced thick steel plate, and some elasticity of the seal was required. For this reason several kinds of seals were tested, and Viton was selected. Some cooling was required to prevent destruction of the seal. On an industrial unit the tightness would be ensured by bright-parts making possible more efficient cooling of the seal.

Mixing of the reactants : in the pilot reactor the liquid was sprinkled on the tyres places in a fixed position in the basket. Another way of contacting could consist either in sprinkling the liquid through a rotating sprinkler or making the basket rotate slowly in order to improve the mixing of the reactants. Some mechanical mixing is required in the rubber dissolving.

Main pump characteristics : when depolymerization occurs gas evolves in the bulk liquid circulated with the main pump. The presence of the gas might drop or stop the sucking action of the pump. This problem has been fully solved by focusing attention on the pump characteristics and its proper location in the loop.

Heater : no special attention except the observation of a sufficient liquid velocity. After several months of batch operations clean pimpes has been found.

2.3.3. Products characteristics (16).

Various oils can be used as long as they are available at low price and have a moderate amount of volatile compounds below 380° C. Beside waste oils which can be used, two kinds of oil have been systematically explored : aromatic extracts and heavy fuel oil of the market. Various tyres have been treated : car tyres, truck tyres and earth work tyres.

Pyrolysis gas, rich in methane and saturated molecules, has an average molecular weight of 45.3 g and a heat value calculated of 10 400 kcal/kg.

The characteristics of gasoline have been given in chapter I ; the variable composition is due to altogether rubber depolymerisation and cracking of the oil.

The fuel-oil product corresponds to when the contacting oil has dissolved the rubber and contains no more gasoline and gas.

It is very interesting to compare the analyses of the fuel oil obtained to those of the corresponding contacting oil, table 12 (chapter I).

The thickening effect of the depolymerised gum dissolved is largely compensated for by the diluent effect of the middle distillate recycled back to the fuel oil after each operation.

It should be borne in mind that these middle distillates come essentially from rubber depolymerisation into oligomers and also from some cracking of the oil.

As it can be seen above the finely dispersed carbon black increases the Conradson Carbon of the corresponding feeds by about 5 absolute percents. No decantation of the carbon black was ever observed in all the liquid fuel oils obtained.

The resultant fuel was burned with success in a 6 300 MJ/h boiler. The carbon black did not affect the quality of the smoke. More, the sulphur content is lower than in contacting oil.

The operating conditions enable viscous fuel oils to be valorized by decreasing their viscosity and pour point as the result of oligomer formation and the additional cracking of the hydrocarbons.

2.3.4. Technical and economical discussion (35).

The large size pilot plant described above gives a most representative view of what an industrial unit will be.

For economic reasons a batchwise process requires paying special attention to the streamtime with regard to the equipment cost. For this reason it may be more advantageous to associate a couple of reactors timed so that only one heater could be used twice a shift. Each oil batch feedstock is preheated by the fuel oil produced in the alternate previous loop which is to cool before storage. One column and a vessel make the light effluents separation. On the other hand the gas and gasoline produced can be used on the site to feed the heater.

Concerning storage it would be most advantageous to have several tanks for the various possible contacting oil.

Advantages of the process is the feasibility to treat whole tyres (cars, trucks, earthwork vehicules) so that shredding is not longer necessary. The trickling contact between oil and tyres involves moderate holdup of the liquid and shortens the time required for heating and cooling the bulk liquid. Practically any kind of hydrocarbone can be used as long as the oil doesn't distill too much before 360° C or so. Various rubber wastes can be treated such as composite metallic and rubber parts from the transport vehicule industry. This latter case is of great interest for recovering the metallic portion.

On the passenger car tyres basis the recoverable energy can by calculated. Metallic waste with some undissolved tyre constituents are 22 Wt % of tyres. Tyre fraction equivalent to proces utilities consumption is 14.5 Wt % and undissolved wastes (depending on the aromaticity of the oil feed) Wt 3.5 %. Then, the recoverable fraction is Wt 60 %. Based on capacity 8 000 t/y crude waste tyres, energy balance can be summarized (table 25).

Basis	8 000 ton/y
Recoverable fraction	4 800 ton/y
*TOE recovered	4 176 TOE/y
TOE recovered per ton	0.52
Investment	11.10^6 FF
Investment per ton	2 600 FF

* Ton Oil Equivalent

Table 25 - Energy recovery (35).

Including gas storage and booster, but excluding cost of feedstocks storage and tyres handling which can be largely dependent on existing facilities of the site, the investment cost approximates FF 11 millions (U.S. dollars 1,4 millions) for capacity of 8 000 tons/year (stream factor : 8 000 hours/year ; batch durations 4 hours, batches/shift : 2).

The operating cost (table 26) includes a capital total charges of FF 145/ton of produced oil assuming a payback time of 3 years before taxes and giving a rate of return on investment capital after taxes of 16 % . It is supposed also 15 opetators ; the energy consumption is 1797 kWh/day for electricity and 5,28 tons/day for steam ; gas and gasoline fit the heater energy requirement. The contacting oil/tyres ratio is 3. Waste produced have not been rated.

	Operating cost	
	K FF/year	FF /ton of produced oil
Fixed Costs		
Capital to depreciation	3 700	126
Working capital	560	19
Maintenance + Insurances	660	23
Direct labour	1 800	61
Running costs		
Electricity (2 FF/kWh)	120	4
Steam (144 FF/ton)	250	9
TOTAL	7 090	242

Table 26 - Operating costs (35).

The minimum sale price of produced oil giving the above payback time and rate of return corresponds to the total operating cost plus the feed oil and waste tyres prices per ton of produced oil applying the above yields.

If the sale price of the produced oil is given, the maximum purchase price of feed stocks can be calculated assuming same payback time and rate of return.

For instance, it can be shown that if both the contacting oil and the produced oil are priced at the number 6 FO of FF 1 600/ton the waste tyres cost cannot be higher than FF 170/ton.

2.4. Kutrieb Corporation Process (36).

Principe - Process description - Products characteristics.

Kutrieb Corporation, Chetek, Wisconsin, has sold a tire pyrolysis plant to Bergey's, Inc., Franconia, Pennsylvania. The plant, which has a design capacity of 500 lb of tyres per hour (or 1,500 TPY), is presently in the startup mode. The process can accept whole tyres in a batch mode with a targeted cycle time of 3 hr. To satisfy the Pennsylvania state regulations for scrap tire storage, the tires are cut in half circumferentially. The tyres are loaded into the reactor chamber, the loading door is closed airtight, the reactor is purged with uncondensed gas from the condenser, and the reactor is heated to about 800° F by externally fired, multifuel burners. Recycled oil and gas from the pyrolysis process are burned simultaneously. The reactor operates with a slight vacuum of about 1 inch of water. The only oxygen present in the reactor is that which occupied the air space at the time of loading. Consequently, the pyrolysis reactions occur under reductive conditions.

The pyrolysis vapors are condensed in an air-cooled condenser for storage as fuel oil (yield, 35 %), while the gas is compressed and the stored as fuel gas (yield, 20 %). The oil has a sulfur content of about 1 %, a water content of about 1.1 %, an ash content of 0.01 %, and a heating value of 17,000 to 18,000 Btu/Ib. The gas has an estimated heating value of 0.127 gallon of oil equivalent per pound of gas, or about 1,033 Btu/scf.

After a cycle is complete, the solid residue is cooled down to 200° F and then pushed from the reactor by a ram. A pair of compression rollers breaks the char into samller particles. Some bead steel (yield, 5 %) and fabricare separated by a vibrating grate ; smaller steel pieces than are separated magnetically and are available for sale as scrap. Much of the cord is not pyrolyzed and remains in the char. The results of independent testing of the char (yield, 38 %) as a rubber filler indicate that the char particle size is larger than for commercial carbon black, giving a poor dispersion rating, and that the tensile strength and initial modulus are significantly reduced. The ash content is about 15 %, the sulfur content is about 3.5 %, and the heating value is 12,480 Btu/Ib. The operator is presently pursuing methods of upgrading the char to improve its marketability.

The utility requirements are less than 4 kW of electricity, no cooling water, and 15 % of the product oil and gas as process fuel. The net energy recovery for the process is estimated by the process developer to be about 80 % assuming 500 Lb of tires processed per hour, a char heat value of 14,309 Btu/Ib, as stack heat recovery of 6,9 gal of oil equivalent, a gas heat value of 1,033 Btu/scf, an oil density of 7,5 Ib/gal, and process yields of 35 % oil, 20 % gas, and 38 % char. The actual analyses of the char heat value is only 12,500 Btu/Ib, or about 13 % lower than that assumed.

Kutrieb assumes that the oil and gas produced by their process as well as waste oil would be used as fuel in their multifuel burners to produce process heat, steam, or electricity. If all the oil and gas produced from 500 Ib of tires per hour is used for steam and electrical generation, 125 kW could be generated. They claim that as many as six pyrolysis units could be ganged together and operated from two control centers. Such an arrangement could produce up to 750 kW of electricity and could be custom sized for a particular location.

Kutrieb has selected the batch mode rather than the continuous mode of operation for their process primarily because they believe the fire safety problems associated with a continuous supply of oxygen entering the reactor with the rubber feed and the potential escape of a low flashpoint liquid with the continuous solids removal are minimized in their batch process.

Potential uses of the product char are expected by Kutrieb to include a fuel as a coal substitute and a filler black for off-road tires.

3. CONCLUSION.

Since 1968, a large number of tyre pyrolysis projects incorporating a broad range of process technologies have been carried out with laboratory, pilot-plant, and small commercial-size equipment. Most investigators found rubber pyrolysis to be technically feasible, and several commercial projects in the United States, Japan, Great Britain, West Germany, and France are under construction, in startup, or in operation.

Pyrolysis processes are either oxidative or reductive depending on the atmosphere within the reactor. Process data vary considerably. Reactor temperatures range from 460 to 1 830° F. Reactor types vary from retorts, rotary kilns, fluidized beds, conveyor kilns hot oil baths, molten salt baths, arc plasma, to microwave ranges.

It appears that tyre pyrolysis is a technologically effective method of reclaiming some energy, some petrochemical products, and other products from the large numbers of tyres. But product quality and value are uncertain.The pyrolytic oil, if unseparated, is approximately equal in value to N° 6 fuel oil. If fractional condensation is used to produce more than one cut, values can be significantly improved. The gas is not pipeline-grade gas and cannot be commercially marketed. The char contains carbon, ash, sulfur, and nonvolatile hydrocarbons. However, the carbon must be refined further to obtain carbon black of saleable quality. Most of the data suggest that the carbon black is only on SRF grade and not suitable for reuse in tread rubber.The steel is considered scrap.

Four pyrolysis processes are technically very advanced : Tyrolysis, DRP, UTC-IFP and Kutrieb processes. Their commercial development will depend obviously on the economical faisability.

The future of the Tyrolysis process does not seem certain because of the importance fo the investment costs, the size of the unit which increases the collection costs, the lack of valorization of the pyrolysis products.

The lack of economical data on the Kutrieb process does not permit to discuss its commercial development. But its running is well adapted to little unities (5 000 to 15 000 t/y) and possibility of treating whole tyres : these adavantages balance the drawback of the indirect heating.

The two others processes, DRP and UTP-IFP, appear technically and economically more efficient. They are different and complementary. DRP process runs continuously with a well known technology (fluidized bed). It accepts all types of organic wastes, what may reduce the collection costs. Its investment costs are moderated.

UTC-IFP process runs by batch with a sample and hardy technology. It is especial for rubbers and tyres and can treat without shredding big size tyres. Its heating method is original and realized by direct contact with an heavy hydrocarbon which renders soluble the degradation products and the whole can be recycled.

It is the alone processe able to treat rubber-metal composites to recover metallic pieces the cost of which is often very high (car industry). Its investment costs are low and the rentability can be reached by small size facilities (5 000 to 10 000 t/y).

III. GENERAL CONCLUSIONS AND RECOMMENDATIONS

This study has tried to show the state of the current knowledge in the field of the pyrolysis of rubbers and tyres. During the last ten years considerable progresses have been made from the scientific and technological points of view.

Nowadays, the basic data required for the processes development are sufficient.

The production of valorized chemicals is limited ; the carbon black is not easily recyclable and the mainly aromatic oil is a complex mixing. The development projects have been numerous and the technical and economical compelling has permitted to screen the processes, in a same time simple, able to treat whole tyres, adjusted to small size unities (5 000 to 10 000 t/year). Then, it does not seem necessary to develop researches on the alone theme of the pyrolysis processing. But complementary studies will be profitably undertaken, or to optimize the valorization of the pyrolysis products coming from the test processes, or to promote a new and more efficient solution, by exemple at middle distance between pyrolysis and reclaiming.

1. VALORIZATION OF THE PYROLYSIS PRODUCTS.

From existing processes in industrial development, it is necessary to consider more profitable uses of pyrolysis products than their combustion, like :

- the craking of the pyrolysis oil to isolate the light aromatics (especially benzene, toluene, styrene, ethylbenzene) in the DRP process,

- the recycling of the carbon black in the making of low quality rubber, paints and inks (DRP process),

- the recycling of the balck carbon-oil suspension in low quality making (process UTC - IFP),

- the pyrolysis of specific rubbers (fluorated, siliconated...) especially entering in the composition of metal-rubber composites in the aim of metallics pieces recovery.

The recycling of these products may be check by the users' conservation and they must be made sensitive and concerned by these studies because they will be in charge of the following promotion.

2. NEW WAYS OF VALORIZATION OF THE RUBBER AND TYRES WASTES.

The pyrolysing of this waste is a progress in regard of the direct combustion but the resulting recycling is limited.

These limits depend on the principe of the process which makes a thermal cracking of organic fraction of the materials. So, rubbers and tyres lose all their properties during this treatment. A too destructive pyrolysis does not permit the recovery of easily reusable raw materials. Considering the present knowledges, an axis of research would be to exam the posibility of restoring the original elastomer by selective devulconizing. It was the aim of old reclaiming processes which have been regressed for several years. Nevertheless, regarding the conservation of the energy content of the rubber waster, the reclaiming process reachs an efficiency of 78 % from crumb rubber. The raw material generally used for reclaiming is a retreading crumb rubber but the treatments of reclaiming are not profitable presently. The reasons of this profitability are the loss of selectivity of the reclaiming process and the incomplete devulcanizing. Theses processes have not progressed for several years.

To obtain a good reclaim, the rubber structure must be entirely devulcanized without damaging of elastomer-macromelecules, what would be operated by micro-waves, biological degradation controled thermal degradation with or without chemical reactants. If the two first methods appear today futuristic, the third way seems more quickly feasable, considering the results of

J.M. BOUVIER and Co (11) : the devulcanizing speed is quick at low temperature (240 - 260° C) but the degradation cinetic of macromolecules is very slow and the deterioration of the elastomer is negligible. By exemple, the making of a recycled paste could be tried by pre-inflating of the material in presence of its extender oil and thermal devulcanizing treatment ; the use of this poste could tested on rubber or road making asphalt industries. By UIC-IFP technics, this experiment could concern the recovery of whole tyres. Accounting the limitation of the pyrolysis for the recycling of raws material, it seems necessary to research an intermediary valorization, nearer to the regeneration, able to conserve the function of the material, i.e. to recycle the charged devulcanized elastomer.

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