



(51) International Patent Classification: Not classified

(21) International Application Number:
PCT/GB2009/002343

(22) International Filing Date:
1 October 2009 (01.10.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PI 0804234-9 1 October 2008 (01.10.2008) BR

(71) Applicant (for all designated States except MW, US):
PETRÓLEO BRASILEIRO S A - PETROBRAS [BR/BR]; Av. Republica do Chile, 65, Rio de Janeiro (BR).

(71) Applicant (for MW only): **BENSON, John, Everett** [GB/GB]; 14 South Square, Gray's Inn, London WC1R 5JJ (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **DE CASTRO, Luiz Depine** [BR/BR]; Av. Nossa Senhora de Copacabana, 126, Ap. 401, CEP-22020-001, Rio de Janeiro, RJ (BR). **DE CASTRO DUTRA, Carlos, Henrique, Monteiro** [BR/BR]; Rua Ituverava, 136, Ap. 1002, Anil, CEP-22750-006, Rio de Janeiro, RJ (BR). **DE FREITAS, Luiz, Clóvis** [BR/BR]; Estrada General Leônidas Cardoso, 1874, C/9 Barra de Guaratiba, CEP-23022-820, Rio de Janeiro, RJ (BR).

(74) Agents: **BENSON, John, Everett** et al.; J.A. KEMP & CO., 14 South Square, Gray's Inn, London WC1R 5JJ (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

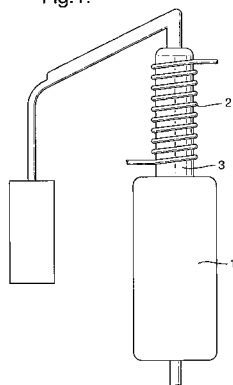
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: PROCESS FOR THE DISTILLATION OF DECANTED OILS FOR THE PRODUCTION OF PETROLEUM PITCHES

Fig.1.



(57) Abstract: This invention describes a process for the distillation of decanted oil to improve the efficiency of the production of pitches having excellent physical and chemical properties through the development of a distillation process which basically comprises the introduction of a stage of condensation of light volatile compounds derived from distillation of the decanted oil, causing these light compounds to be recycled to the hot zone of the still and react with the raw material acting as a solvent phase which has a lower viscosity than the reaction system, within a particular temperature range and for a particular time.



**PROCESS FOR THE DISTILLATION OF DECANTED OILS FOR THE
PRODUCTION OF PETROLEUM PITCHES**

FIELD OF THE INVENTION

This invention has scope for application in the processes for the distillation of decanted oil with the aim of increasing the production yield and quality of the pitches obtained.

BACKGROUND TO THE INVENTION

Pitches are used for the production of carbon artefacts, especially for the production of carbon fibres having excellent mechanical properties. They also have application as binders in the industries for the production of anodes, aluminium and graphite electrodes for the steel industry.

The manufacture of pitches conventionally uses coal tar as a raw material.

However, environmental problems deriving from the use of coal tar, the instability in the supply of this raw material and the great variations in the price of this item has awoken industry's interest in alternative sources of raw material originating in the heavy residues of oil processing.

Conventionally the production of pitches from decanted oil involves a processing stage in which the raw material is distilled with removal of the lighter compounds, leaving as the end product a pitch which has solid properties at ambient temperature. The mean yield from a conventional process such as that described above is approximately 20% of pitch.

RELATED ART

Document US 4,705,618 [Maruzen Petrochemical Co., Ltd.], included here as a reference, describes a process for the continuous preparation of a "virtually" optically isotropic and substantially uniform pitch intermediate for the manufacture of a pitch binder for the preparation of carbon fibres, which comprises

heating the heavy oil containing a quinoline-insoluble fraction of less than 5% by weight selected from a group which can be selected from tars from various origins having coal as a base, by-products of naphtha cracking, by-products of diesel cracking and decanted oils in a tubular heater at particular pressures and temperatures, for a particular residence time. The flow from this heater is transferred to a distillation column where it is distilled at a specific pressure and temperature so that the light fractions derived from the heavy fraction are separated out as product from the top of this column and the heavy fraction is collected from the bottom of the column as an intermediate pitch.

Document US 4,820,401 [Koz Iizuka, Maruzen Petrochemical Co., Ltd.], included here as a reference, discloses a process for the preparation of a pitch with a softening point below 350°C for the manufacture of high performance carbon fibres which comprises subjecting a heavy oil from oil or coal or a heavy component obtained from that heavy oil by distillation to heat treatment or hydro-treatment in a tubular heater under pressure for a particular residence time. In a second stage, a monocyclic aromatic hydrocarbon solvent is added to the heat-treated material and the new insoluble component formed is recovered essentially as a high molecular weight isotropic bituminous material. In a third stage the previously obtained bituminous material is subjected to hydrogenation treatment at a particular temperature and pressure with the addition of a solvent based on a hydrogen donor, essentially yielding an isotropic hydrogenated pitch and finally, in a fourth stage, the compound from the third stage is subjected to heat treatment in a temperature range from 350°C to 500°C under a pressure above atmospheric to convert it into a pitch binder.

Document US 4,931,162 [Conoco Inc.], included here as a reference, discloses a process for the preparation of a pitch suitable for the production of high-quality

carbon fibres which comprises distillation from a feed containing aromatic compounds, an aromatic distillate free from monophase resins having an initial boiling point of 390°C at atmospheric pressure. The distillate is subjected to particular temperatures for a time, at atmospheric pressure, so as to obtain a distillate free from mesophases, but containing a percentage of at least 5% of mesophase resins. The free distillate is also subjected to temperatures in the range from 370°C to 420°C under atmospheric pressure for a particular time in the presence of an inert gas in order to convert the latter resins into a pitch binder.

Document US 5,032,250 [Conoco Inc.], included here as a reference, discloses a process for the preparation of a pitch binder which comprises combining an isotropic pitch containing mesogens with a solvent, then performing a phase separation of the mesogens with solvent under supercritical temperature and pressure conditions in such a way that these mesogens are associated with the solvent to form a pitch binder, which is recovered.

US 5,259,947 [Conoco Inc.], included here as a reference, discloses a solvated mesophase pitch having a liquid-crystalline structure comprising a vehicle of mesogens, pseudo-mesogens or a mixture thereof in which the solvated mesophase pitch is at least 40% by volume optically anisotropic and in which the solvated mesophase pitch melts at at least 40°C below the mesogen component or in which the solvated mesophase pitch contains pseudo-mesogens, where the solvated mesophase pitch melts or softens and the pseudo-mesogen component does not; where the solvent dissolves in the mesogen or pseudo-mesogen and gives rise to a lower melting point when it retains a substantial volume of liquid-crystalline structure.

From what it is possible to learn from the representative examples of the state of the art described above, in almost all if not all of these there is a need to control temperature, but the

temperatures are generally very high. Likewise it is not infrequent that the processes have to be carried out at a pressure above atmospheric. On the other hand it will be noted that light fractions are effectively removed from the process and in almost all there is the need to introduce a solvent in order to obtain the pitch. Finally it will be seen that concern lies with the physical and chemical qualities of the pitch for the production of carbon fibres, but not with the efficiency of the process as such.

SUMMARY OF THE INVENTION

This invention relates to a process for the distillation of decanted oil in order to increase the yield of the production of pitch binders with excellent physical and chemical qualities which makes them suitable for use in various industrial applications.

The above aim has been accomplished through developing a distillation process which basically comprises the introduction of a stage of the condensing the light and volatile compounds deriving from the distillation of decanted oil, these light compounds being recycled to the hot zone of the still where they react with the raw material forming a mixture which has less viscosity than the reaction system, which acts as a solvent phase. This stage is carried out at a particular temperature and for a particular time.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a diagrammatical view of the distillation system according to this invention.

Figure 2 shows a graph of heating in a first distillation experiment with a cooling coil according to this invention, in which graphs of the temperature within the still and the temperature at the top of the distillation column are plotted.

Figure 3 illustrates a graph of heating in a second distillation experiment with a cooling coil according to this invention, in which graphs of the

temperature within the still and the temperature at the top of the distillation column are plotted.

Figure 4 illustrates a graph of heating in a third distillation experiment with a cooling coil according to this invention, in which graphs of the temperature within the still and the temperature at the top of the distillation column are plotted.

Figure 5 shows a graph of heating in a fourth distillation experiment with a cooling coil according to this invention, in which graphs of the temperature within the still and the temperature at the top of the distillation column are plotted.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to a process for the distillation of decanted oil with a view to increasing the production yield of pitches having excellent physical and chemical properties.

As already mentioned previously, pitches can be produced using coal tar and heavy oil residues. Heavy oil residues or residues from its processing have been widely used as a primary material for obtaining pitches. However, the majority of the technical work which uses petroleum pitch in its experiments mentions the use of commercial pitches as a raw material. The production of pitches from decanted oil as raw material involves a distillation which removes lighter compounds and makes it possible to form a heavy material, a pitch which is in the solid state at ambient temperature. The yield of pitch obtained from conventional distillation is of the order of 20%. A vacuum which although accelerating the distillation process also results in even lower yields than in the conventional process may be applied during distillation.

On conducting a first experiment in the course of bench research for the development of this invention a set-up with conventional equipment was used, with a system for heating the column which made it possible to accelerate the removal of light volatile compounds,

together with thermal insulation to prevent the loss of heat to the exterior. The results are shown in Table 1 as "Run 1" below.

The abbreviations common to all the tables in this report need to be explained, to provide a better understanding:

T_{int} - internal temperature of the still,

T_{top} - temperature of the top of the distillation column,

Time - distillation time,

Y_{Pitch} - yield of pitch,

SP - softening point,

TI - compounds insoluble in toluene,

QI - compounds insoluble in quinoline.

A second experiment was then performed in which the distillation column was not heated. The results are shown as Run 2 in Table 1 below.

TABLE 1

Distillation	T_{int}	T_{top}	Time	Y_{Pitch}	SP	TI	QI
	max (°C)	max (°C)	(h)	(%)	(°C)	(%)	(%)
Run 1	485	454	2.5	25.6	85	6.3	0
Run 2	485	427	2.7	29.4	92	9.3	0.7

It was noted that lack of heating for the column resulted in an increase in the yield of pitch, although with similar heating parameters. These results led to the construction of a still (1) of larger capacity with an associated stove (11) for heating. Said still (1) was equipped with a reflux system comprising a coil (2), preferably of copper, surrounding a distillation column (3). A cooling fluid, which can be selected from water, compressed air or any other fluid capable of exchanging heat, flows through coil (2). The still described above can be seen as a diagrammatical illustration in Figure 1.

As already mentioned above, the process according to this invention is based on heat treatment with

reflux.

Heating of the decanted oil and reflux allows light molecules which would be withdrawn from the system by being volatilised to return and remain within the still. This reduces excessive condensation of the heavier molecules, purely because of the presence of these lighter molecules which have considerable aromaticity and naphthenic hydrogens which improve the physical and chemical properties of the pitch.

Heat treatment under reflux almost completely decomposes the paraffin fractions, bringing about dealkylation of the alkyl-aromatics, as well as condensation of the aromatic components, especially the lighter fractions.

In this way a more uniform distribution of the components can be obtained in order to increase the yield of pitch, bringing about an increase in toluene-insoluble (TI) compounds without excessively raising the softening point (SP) of the pitch.

Distillation of decanted oil with the application of reflux in this way inhibits the volatilisation of low molecular weight components, and causes them to condense out. These compounds, which have a low molecular weight, on the other hand form a solvent phase which has less viscosity than the reaction system. In this way these low molecular weight components inhibit fast condensation of the components of greater molecular weight, help break the chains in the latter components, an action which delays the formation of quinoline-insoluble compounds, and also almost entirely eliminate the need to introduce external solvent compounds into the system.

The still as constructed was used in a further four experimental runs for which results are shown in Table 2 below, with an indication of whether reflux (Ref) is used or not.

TABLE 2

Distillation	T _{int} max (°C)	T _{top} max (°C)	Time (h)	Y _{Pitch} (%)	SP (°C)	TI (%)	QI (%)	Ref
Run 3	445	309	3.4	36.9	104	9.3	1.1	None
Run 4	435	293	9.3	42.0	95	11.0	1.3	water
Run 5	433	263	7.8	49.3	83	14.3	1.8	water/ air
Run 6	432	272	9.0	53.3	86	17.8	2.4	Air

The experiments for which values are illustrated in Table 2, also known as Runs, will be described below:

In order to carry out Run 3, 7580 g of decanted oil was placed in a still (1) prepared according to this invention, equipped with a distillation column (3) fitted with a coil (2). Distillation was started, but without cooling distillation column (3), coil (2) remaining unused. Distillation continued for three hours and twenty-five minutes. The maximum temperature (T_{int}) in the still reached 445°C. The maximum temperature at the top of the distillation column reached 309°C. With these parameters and this technique a yield of 36.9% of pitch was obtained. Figure 2 illustrates the heating graph for this Run 3 in which the change in the temperature of the still (T_{int}) is plotted on the graph in the form of lozenges and the change in the temperature at the top of the column (T_{top}) is plotted in the form of triangles.

In order to carry out Run 4, 7580 g of decanted oil was placed in a still (1) prepared according to this invention, equipped with a distillation column (3) fitted with a coil (2). Distillation was begun with cooling of distillation column (3) using water as the cooling fluid in coil (2), and the temperature in the still (T_{int}) stabilised at 377°C. Distillation continued with reflux for seven hours, after which the flow of cooling water was interrupted and the distillation

process was allowed to continue for a further two hours and twenty minutes. The maximum temperature in the still (T_{int}) reached 435°C. The maximum temperature at the top of the distillation column reached 293°C. With these parameters and this technique a yield of 42.0% of pitch was obtained. Figure 3 illustrates the heating graph for this Run 4 in which the change in the temperature of the still (T_{int}) is plotted on the graph in the form of squares and the change in the temperature at the top of the column (T_{top}) is plotted in the form of solid circles.

In order to carry out Run 5, 7540 g of decanted oil was placed in a still (1) prepared according to this invention, equipped with a distillation column (3) fitted with a coil (2). Distillation was begun with cooling of distillation column (3) initially using water as the cooling fluid within coil (2), and the temperature within the still (T_{int}) stabilised at 376°C. Distillation continued with reflux for three hours and thirty-eight minutes, after which the flow of cooling water was interrupted. The distillation process was extended for a further forty-five minutes and then compressed air was used as the cooling fluid for a further two hours. After this time cooling of distillation column (3) was interrupted and distillation continued for a further one hour and ten minutes. The maximum temperature within the still (T_{int}) reached 433°C. The maximum temperature at the top of the distillation column reached 263°C. With these parameters and this technique a yield of 49.3% of pitch was obtained. Figure 4 shows the heating graph for this Run 5 in which the change in the temperature within the still (T_{int}) is plotted on the graph in the form of squares and the change in the temperature at the top of the column (T_{top}) is plotted in the form of solid circles.

In order to carry out Run 6, 7480 g of decanted oil was placed in a still (1) prepared according to this invention, equipped with a distillation column (3)

fitted with a coil (2). Distillation was started with cooling of distillation column (3) using only compressed air as the cooling fluid. Distillation continued with continuous cooling of distillation column (3) throughout the eight hours of the process. The temperature over these eight hours gradually and slowly rose until the maximum temperature within the still (T_{int}) reached 432°C . Heating was continued for a further hour. Figure 5 shows the heating graph for this Run 6 in which the change in the temperature within the still (T_{int}) is plotted on the graph in the form of squares and the change in the temperature at the top of the column (T_{top}) is plotted in the form of solid circles.

As will be seen, using a process according to the invention it has been possible to obtain a yield of the order of 53.3%.

Although this invention has been described in the form of its preferred embodiment, the main concept underlying this invention, which is a process for the distillation of decanted oil with the object of increasing the efficiency of the production of pitches having excellent physical and chemical properties rendering them suitable for use in various industrial applications, including the manufacture of carbon fibres, retains its innovative nature, while those skilled in the art may envisage and make variations, modifications, changes, adaptations and the like which are necessary and compatible with the method of working in question without however going beyond the spirit and scope of this invention which is represented by the following claims.

CLAIMS

1. Process for the distillation of decanted oils suitable for the production of petroleum pitches, which comprises condensation of compounds deriving from distillation of decanted oil, said compounds being recycled to a zone of a still (1), reaching a maximum temperature from 430°C to 435°C for a total distillation time from 7 to 10 hours.

2. A process according to Claim 1, characterised in that still (1) is equipped with a reflux system comprising a coil (2), preferably of copper, surrounding a distillation column (3) and in that a cooling fluid, which may be selected from water, compressed air and any other fluid capable of meeting the heat-exchange capability requirements, flows within the coil (2).

3. A process of distillation according to Claim 1 or 2, characterised in that the recycled compounds satisfy one or more of the following:

react with the raw material,

act as a solvent phase of lower viscosity than that of the reaction system,

inhibit rapid condensation of components of greater molecular weight, assist the breaking of chains in components of greater molecular weight which delay the formation of compounds which are insoluble in quinoline, and

do away with the need to introduce external solvent compounds into the system.

4. A process according to Claim 1, 2 or 3, characterised in that the stage of condensing the compounds is performed by attaching a coil (2) containing a cooling fluid which circulates within it around a distillation column (3) of a still (1).

5. A process according to any preceding claim, in which said compounds comprise compounds that are light and/or volatile.

6. Process for the distillation of decanted oils for the production of petroleum pitches, characterised in that it comprises the introduction of a stage of condensation of the light and volatile

compounds deriving from the distillation of decanted oil which makes these compounds suitable for recycling to the hot zone of a modified still (1), reaching a maximum temperature within the range between 430°C and 435°C for a total distillation time in the range between 7 and 10 hours.

Fig.1.

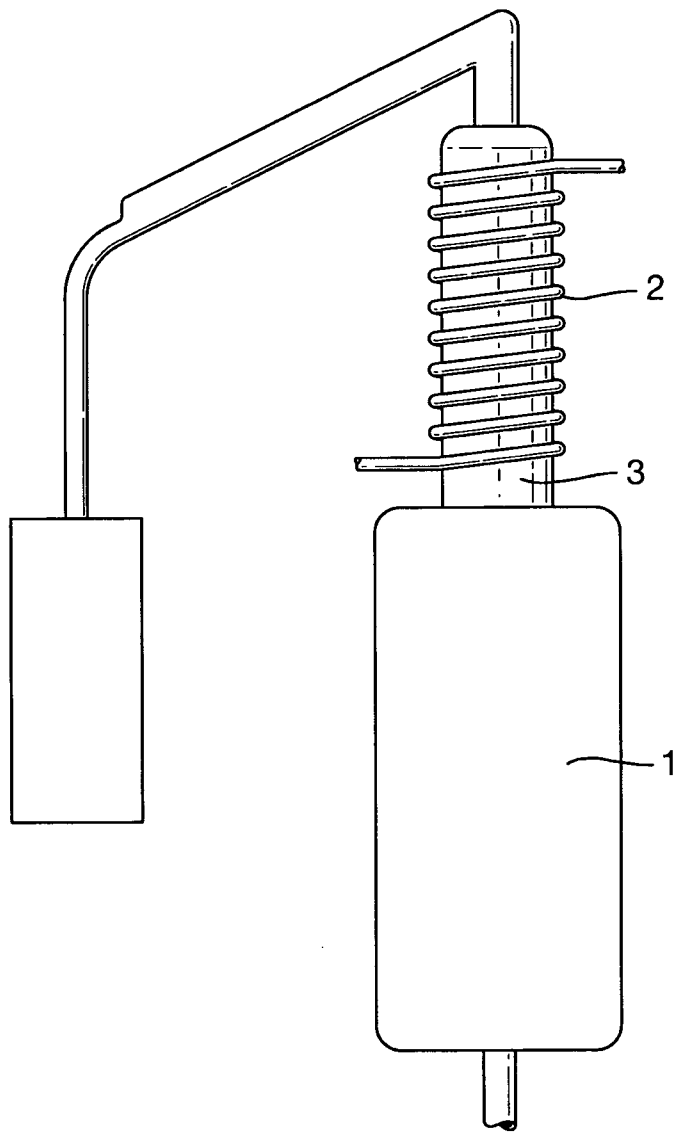


Fig.2.

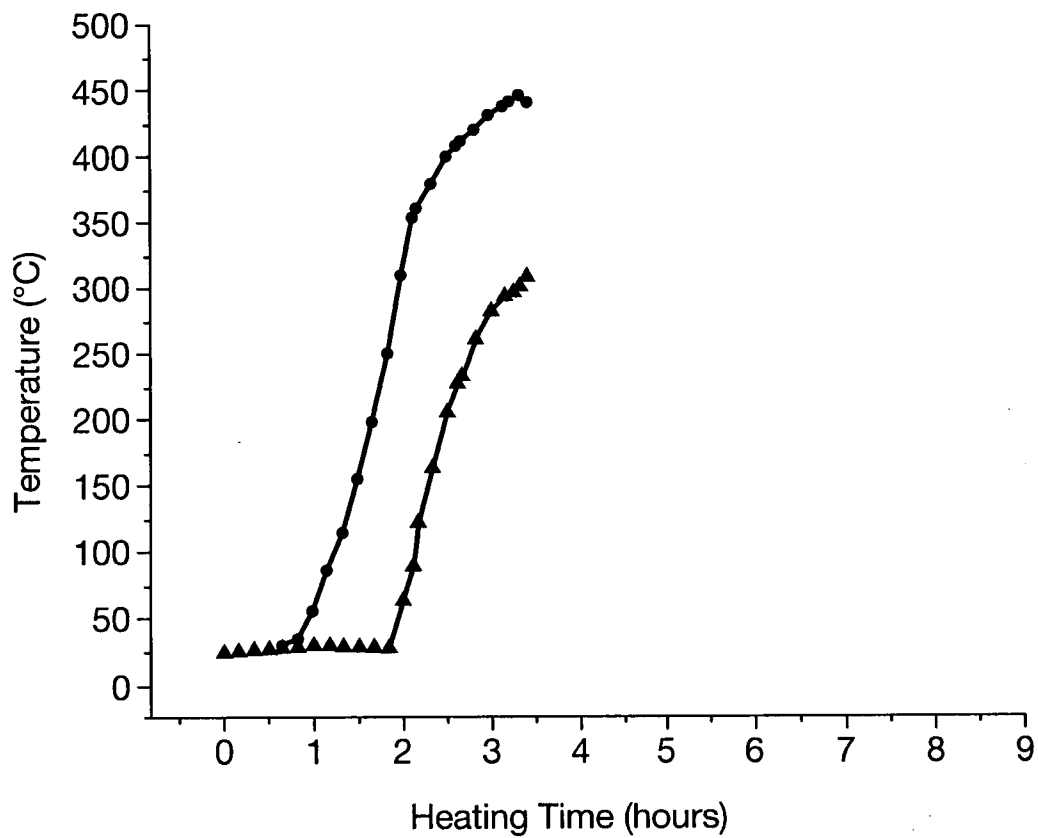


Fig.3.

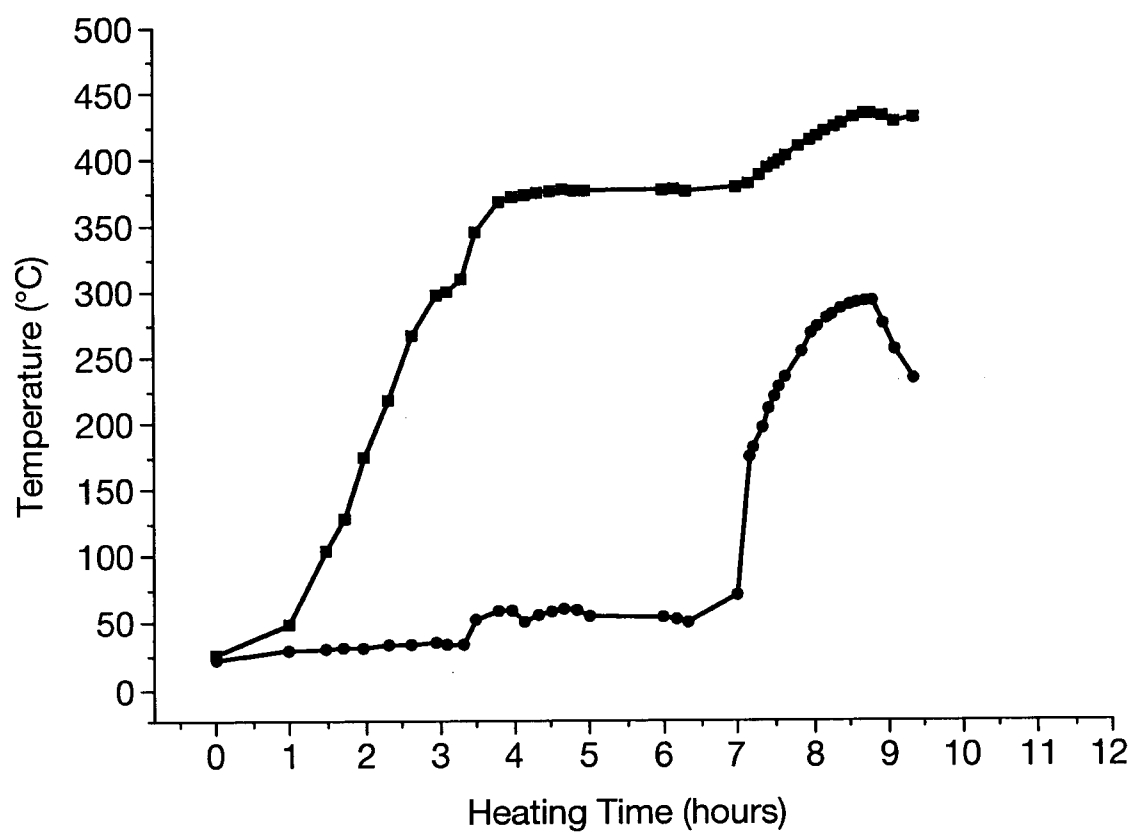


Fig.4.

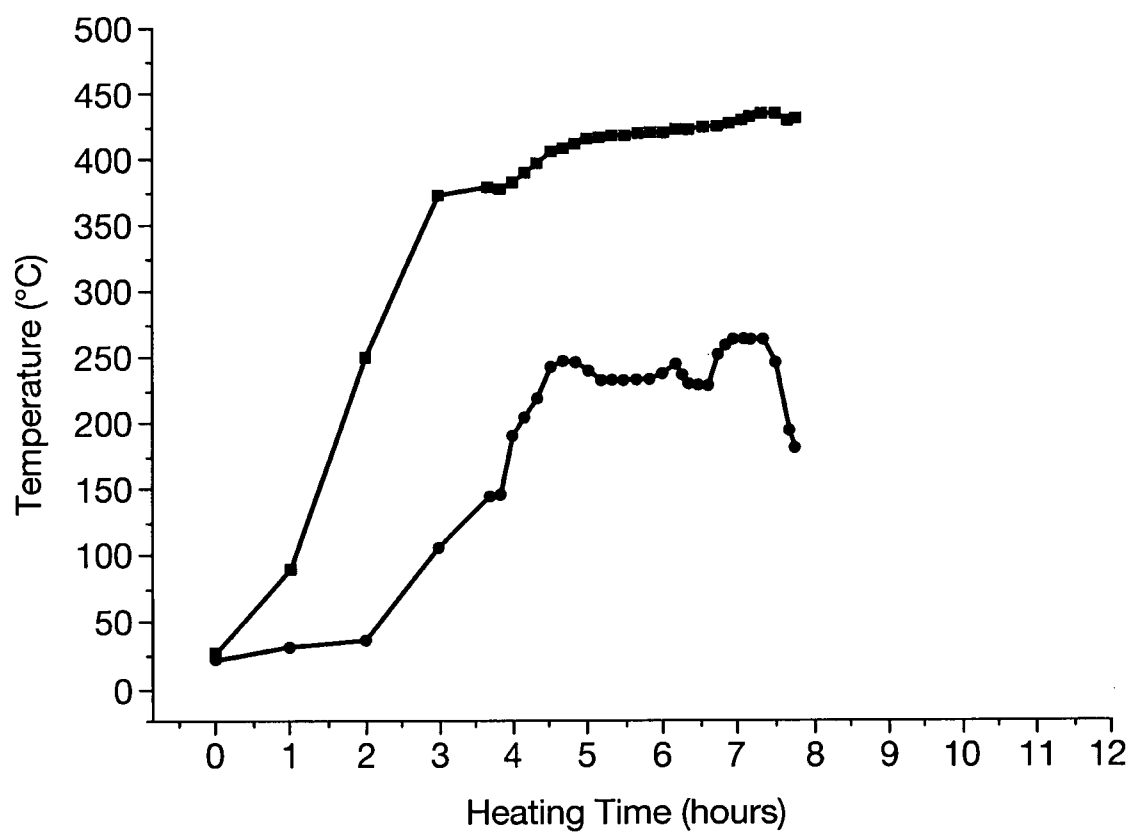


Fig.5.

