THE EFFECT OF THE SUBSTRATE ON THE PITCH WETTING CAPACITY

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Abstract. In this work, the wetting behaviour of a petroleum pitch, modified with a surfactant, and a binder coal-tar pitch against different substrates was studied. The results show that both pitch and substrate have a great incidence on the wetting behaviour, and consequently, in their mutual interactions during the mixing step. Low values of surface tension and viscosity in the pitches lead to lower temperatures of wetting. With the petroleum coke and magnesia the wetting occurs at lower temperatures than with graphite and carbon black, regardless of the pitch used. Moreover, experiences carried out with alumina in different stages of crystallization revealed that the crystalline order greatly affects the wetting. Thus, corundum (crystallized alumina) is wetted, while amorphous alumina (basic, acid and neutral alumina) does not.

Keywords: pitch; filler; wetting; surface energy

1. INTRODUCTION

Coal-tar pitches are widely used in the industry of the granular carbon technology (e.g., carbon anodes for aluminium production, synthetic graphite for electrodes to be used in electric arc furnaces and magnesia-carbon refractories) because their superb binder properties. The preparation of these types of materials usually involves three consecutive steps: the mixing of the filler with the binder, the conforming to a desired shape and finally the curing. The ultimate properties of these materials are primary established during the interactions that take place at the mixing step [refs.]. For this reason, it is extremely important that during the mixing, the liquid wets the solid, allowing an intimate contact between the binder and the filler to be formed.

The capacity of a pitch to wet a filler can be determined by means of a spreading-drop test, consisting of monitoring the evolution with temperature of a droplet of pitch placed on a granular bed of substrate [ref. Fuel]. As the temperature increases, the pitch drop goes by trough different stages, during which the contact angle changes from $\theta > 90$ °, 90 ° > $\theta > 0$ °. There are two critical stages: (i) when the contact angle decreases below 90 ° and the solid/liquid adhesive forces overcome the liquid cohesive forces, allowing the drop of pitch to be spread (wetting temperature) and (ii) when the contact angle becomes 0 °, which means that the pitch was adsorbed by the granular bed, showing a mat appearance (completed penetration temperature). This test was initially developed for determining the affinity of a binder coal-tar pitch for a petroleum coke in the preparation of carbon anodes for aluminium production [ref. Couderc]. However, this test could be extended to other fillers used in the granular carbon technology, such as graphite, carbon black or magnesia.

On this basis, this paper concerns with the interactions between two different pitches (coal-tar pitch and experimental petroleum pitch) and various fillers used in the preparation of carbon anodes and magnesia-carbon refractories. These interactions were established in terms of wetting behaviour and the results obtained were related with the viscosity, surface tension and composition of the pitches and the surface energy of the fillers.

2. EXPERIMENTAL

2.1. Materials used

Two pitches were used in this study: a typically binder coal-tar pitch (CTP-1) used in the refractory industry for the preparation of magnesia-carbon bricks (supplied courtesy of RHI Refractories) and a petroleum pitch (PP-1) produced from a pyrolysis tar at pilot plant scale by REPSOL YPF.

A third pitch with improved wetting capacity was obtained by adding a 5 wt.% of surfactant [ref.] to PP-1. The surfactant, supplied by REPSOL YPF, is a by-product of the petroleum refining industry. The addition was carried out in a stainless-steel reactor at 130 °C for 30 min under stirring. A nitrogen pressure of 0.1 MPa was used in order to prevent pitch components and surfactant from possible distillation. The new pitch was labelled PP-1S.

The wetting behaviour of these pitches was study by facing them up to eight substrates of different composition and/or characteristics: a regular calcined petroleum coke, commonly used in the aluminium industry for the preparation of Söderberg carbon anodes; natural graphite, carbon black and fused magnesia, commonly used in the magnesia-carbon refractory production; and alumina of different crystalinity degree (amorphous and corundum) and properties (acid, neutral and basic alumina).

The main characteristics of the pitches and substrates are summarized in Tables 1 and 2, respectively.

2.2. Pitch and substrate characterization

The pitches were analyzed by standard procedures in order to determine their elemental composition (LECO-CHNS-932 and LECO-VTF-900 analyzers), softening point (ASTM D3104 standard), solubility parameters (toluene-insoluble content and quinoline-insoluble content, Petchiney B-16 series PT-7/79 STPTC and ASTM D2318 standards, respectively), carbon yield (ASTM D4715 standard), surface tension at 160 °C (ASTM D1331 standard) and viscosity in the temperature range of 120-180 °C (Bohlin COV-120 digital rheometer).

The substrates were characterized in terms of elemental analysis (LECO-CHNS-932 and LECO-VTF-900 analyzers), immediate analysis (moisture and ash content according to ASTM D3173 and ASTM D3174 standards, respectively). The MgO content in the magnesia was calculated by ICP-MS. The density and the crystalline parameters of the substrates were determined by helium pycnometry and X ray diffraction, respectively.

2.3. Pitch/substrate wetting test

The wetting behaviour of the pitches against the different substrates was studied by means of a spreading drop test. In this test, a cylindrical pellet of moulded pitch was positioned on a flat bed of substrate sieved to between 100 and 125 µm. The crucible containing the materials was then placed in a horizontal tube furnace purged with gas (air or nitrogen) and heated according to the following temperature/time profile: (i) heating at 300 °C h^{-1} up to 65 °C; (ii) from 65 to 100 °C at 150 °C h^{-1}; and (iii) from 100 °C until the molten pitch completed its penetration into the substrate bed at 20 °C h^{-1}. Two quartz windows at both ends of the tube allowed the progression of the pitch/substrate system to be recorded with a video camera. The video camera was programmed to capture images every 3 min. The images were then processed by an image analysis system, and the height of the pitch drop was recorded as a function of the temperature. Figure 1 shows a scheme of the equipment used for this test.

3. RESULTS AND DISCUSSION

3.1. Pitch/coke wetting behaviour

The pitches used in this study were a typically binder coal-tar pitch (CTP-1) and an experimental petroleum pitch (PP-1), which was designed with the aim of using it as an alternative to conventional binder coal-tar pitches in the aluminium and refractory industries. For this reason, PP-1 was prepared with a softening point similar to that of CTP-1 (112 and 115 °C, respectively). However, the different origin of coal-tar and petroleum pitches clearly reflects the differences between CTP-1 and PP-1 composition (Table 1). The presence of quinoline-insoluble particles (QIs) in the coal-tar pitch is probably the feature that most largely remarks the difference between CTP-1 and PP-1, and consequently their wetting behaviour. These particles are totally absence in the case of PP-1, while in CTP-1 they account for 9 wt.%. It is described that QIs have a beneficial effect on the wetting properties of the pitches [ref.]. This is because they facilitate the effective covering of the substrate particles, at the time, that they prevent pitch from infiltration into the intraparticle substrate pores, which ensures an effective binding of the particles.

It is not surprising, therefore, that when CTP-1 is faced up to calcined petroleum coke in a wetting test (Section x.x), it completes the diffusion through the granular bed at 148 °C (Figure 2), while PP-1 does not penetrate even when the temperature is increased up to 250 °C (Figure 2). In a previous work carried out by elsewhere it has been evidenced that petroleum pitches tend to oxidize at low temperatures [ref.]. This oxidation, which preferentially occurs via aliphatic hydrogen, produces an increase in the surface tension and viscosity of the pitch during the wetting experiment, avoiding the diffusion of the pitch through the petroleum coke bed. In fact, the determination of these parameters at 160 °C, before and after the wetting experiment, shows that the surface tension and viscosity of PP-1 increases from 51 to 58 din cm and from 2800 to 4050 cp, respectively. In the case of CTP-1 the viscosity, determined before and after the experiment, changes from 593 to 1680 cp and the surface tension remains invariable in 50 din cm.

It seems evident, that the use of PP-1 as binder requires the modification of the pitch properties in such a way that its wetting capacity would be improved. This can be achieved by the use of a low-boiling point surfactant [refs.]. Certainly, the addition of 5 wt.% of the surfactant S causes a reduction in both surface tension (51 and 31 din cm for PP-1 and PP-1S, respectively) and viscosity (2800 and 2780 cp for PP-1 and PP-1S, respectively), without significantly altering the other pitch parameters (Table 1) and the microstructure of the pitch derived coke (Figure 3). The use of the surfactant allows PP-1 to reach the appropriate surface tension and viscosity for spreading and flowing through the petroleum coke bed before oxidizing (Figure 2). However, the wetting temperature is higher than in the case of CTP-1, which could be related to the fact that PP-1S exhibits higher values of both viscosity and surface tension.

These results indicate that pitch composition plays an important role in the capacity of the pitch for wetting petroleum coke. But, it cannot be ignored that the properties of the substrate could also have a relevant role in wetting behaviour.

3.2. Wetting behaviour of pitch with graphite, carbon black and magnesia

Graphite, carbon black and magnesia were used in a first approach as substrates to face up against CTP-1 and PP-1S. The selection of these substrates were made on the basis that they are substrates used in the refractory industry for preparing carbon-magnesia refractories.

The wetting curves of CTP-1 and PP-1S when they are faced up to carbon black, graphite and magnesia are shown in Figures 4 and 5, respectively. CTP-1 is able to penetrate into the three substrates. However, the wetting behaviour is dependent upon the type of substrate used. With the magnesia, CTP-1 exhibits a similar wetting curve to that obtained for the petroleum coke (taken as a reference), although the temperature of completed penetration is slightly higher (Figure 4). In the case of the graphite, CTP-1 requires higher temperature to initiate the spreading and diffusion through the granular bed, completing the penetration at 159 °C. A complete different profile is observed when CTP-1 is faced up to carbon black; the pitch drop is maintained until temperatures near to 150 °C, but once the cohesive forces are overcome the pitch rapidly spreads and penetrates in the carbon black, giving a temperature of completed penetration of 159 °C.

The PP-1S pitch follows a similar trend to CTP-1, although spreading and penetration phenomena occur at higher temperatures (Figure 5), as in the case of the petroleum coke. It is interesting to note again the different behaviour observed for the carbon black, which is not wetted by PP-1S even when the temperature is increased up to 200 °C.

3.3. Effect of pre-graphitic and crystalline order on the wetting behaviour

In an attempt to deep into the factors that affect the wetting capacity, CTP-1 and PP-1S were faced up to substrates with different pre-graphitic order (pitch cokes obtained at 500 and 1000 °C) and alumina with different crystalline order (acid, basic and neutral amorphous alumina and corundum).

Orden pre-grafitico y critalino de los sustratos.

The different wetting behaviour observed when using different substrates could be related with the different surface chemical functions. In order to deep into this consideration CTP-1 and PP-1S were faced up alumina and groups, with their structural order. In fact, some authors [ref.] refer the capacity to wet with

Diferencias de la breas

These results clearly indicate that in the interaction pitch/substrate, the substrate plays a relevant role.

DISTINTO COMPORTAMIENTO DE LOS SUSTRATOS. RELACION CON EL ORDEN GRAFITICO Y LA CRISTALINIDAD

3.4. Pitch/alumina wetting behaviour. Influence of the alumina crystalinity

3.5. Comparative study of the wetting behaviour of the coal-tar pitch and the modified petroleum pitch

The lower viscosity and also lower surface tension exhibited by CTP-1 with respect to PP-1S determine in a first approach the lower temperatures of wetting ($\theta < 90$ °) and completed penetration shown by this pitch against the substrates studied (Table 3). However, it is interesting to note that the temperature range between wetting and completed penetration is lower in the case of PP-1S. This means that the petroleum pitch requires higher temperatures to overcome the cohesive forces and so reduces the contact angle below 90º, but once this has occurred the diffusion of this pitch through the substrate bed occurs more rapidly than in CTP-1. This could be related with the presence of insoluble particles (primary QI), which could act as a regulator in the diffusion of the pitch [buscar ref.].

The temperatures of wetting and completed penetration are parameters of special relevance in the carbon granular technology because they determine not only the suitability of the pitch for using as binder, but also the optimum temperature for performing the mixing process. Moreover, it is also especially relevant the amount of substrate that the pitch is able to bind, because this relates with the efficiency of the process and also with the percentage of pitch to be used. The amount of substrate bind by the pitch was calculated from the pellets, consisting of substrate agglomerated with pitch, obtained after the wetting experiment. The weight was then transformed into volume, in order to avoid the effect of the different densities of the substrates. The values obtained shows that the properties of the substrate are more significant than the characteristics of the pitch on the substrate fixation (Table 3). Thus, magnesia and petroleum coke are the substrates that are bind in greater amount by both pitches (> 0.83 cm^3 per gram of pitch), while graphite and carbon black exhibit the lowest values (< 0.52 cm^3 per gram of pitch). Moreover, the diffusion of pitch through these latter substrates takes places in a larger range of temperature than the former, this being more acute in the case of the coal-tar pitch. VOLVER A RELACIONAR CON LA AFINIDAD BREA SUBSTRATO.

4. CONCLUSIONS

Viscosidad y tension superficial de las breas

Energia de superficie de los substratos

Orden cristalino

Cineticas de mojado

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5. REFERENCES

Table 1. Main characteristics of pitches.

Pitch	Elemental Analysis (wt.%)					SP[a]	TI[b]	QI[c]	CY[d]	Iar[e]	η[f]	γ[g]
	C	H	N	S	O							
CTP-1	93.6	4.0	0.9	0.5	1.0	115	33	9	60		593	50
PP-1	93.6	5.5	0.0	0.1	0.8	112	26	0	55		2800	51
PP-1S	93.3	5.9	0.0	0.2	0.6	108	23	0	53		2780	31

[a] Softening point (°C)

[b] Toluene-insoluble content (wt.%)

[c] Quinoline-insoluble content (wt.%)

[d] Carbon yield (wt.%)

[e] Aromaticity index determined by FTIR

[f] Viscosity determined at 160 °C (cp)

[g] Surface tension determined at 160 °C (din cm)

Table 2. Main characteristics of substrates.

Substrate	Composition (wt.%)				d_{He}[a]	XRD[b]		
	Carbon	Ash	Moisture	MgO		d002	La	Lc
Petroleum coke	97.7	0.0	0.0	-	2.06	0.348	8.5	3.2
Graphite	94.4	5.2	0.3	-	2.31	0.337	74.6	45.0
Carbon black	98.1	0.1	0.0	-	1.83	0.361	5.3	1.7
Magnesia	-	-	-	97.1	3.12	-	-	-

[a] Helium density (g cm^{-3})

[b] X-ray difractometric parameters (nm)

Table 3. Pitch/substrate wetting parameters.

Pitch	Substrate	W[a]	P[b]	ΔT[c]	P/S[d]
CTP-1	Petroleum coke	138	146	10	0.83
	Graphite	142	159	20	0.23
	Carbon black	147	153	16	0.52
	Magnesia	137	148	11	0.90
	Corundum	165	194	29	0.33
PP-1S	Petroleum coke	164	166	2	0.84
	Graphite	174	179	5	0.31
	Carbon black	-	-	-	-
	Magnesia	166	170	4	1.07

[a] Wetting temperature (°C)

[b] Temperature of completed penetratrion (°C)

[c] Difference between P and W (°C)

[d] Volume of substrate fixed by 1 g of pitch (cm^3)

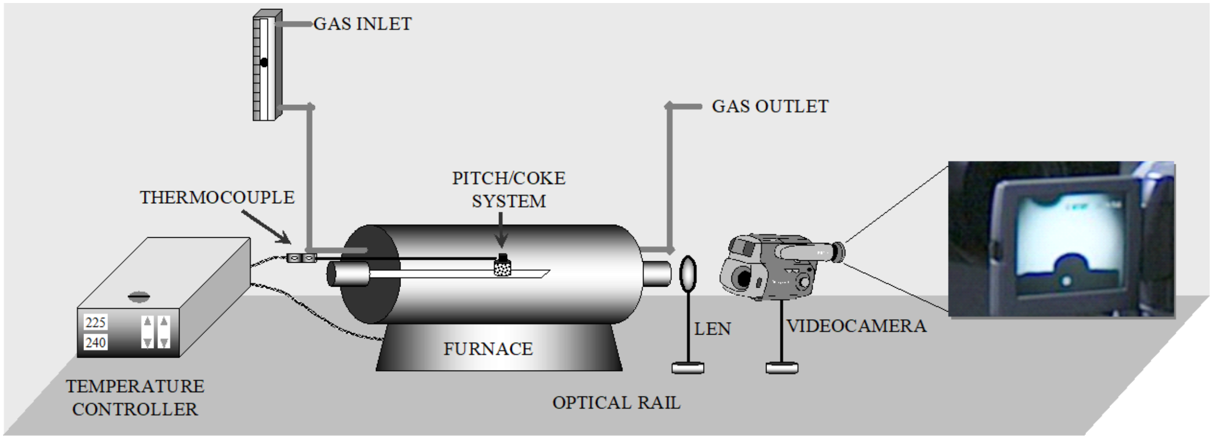

Figure 1. Equipment used for the pitch/substrate wetting test.

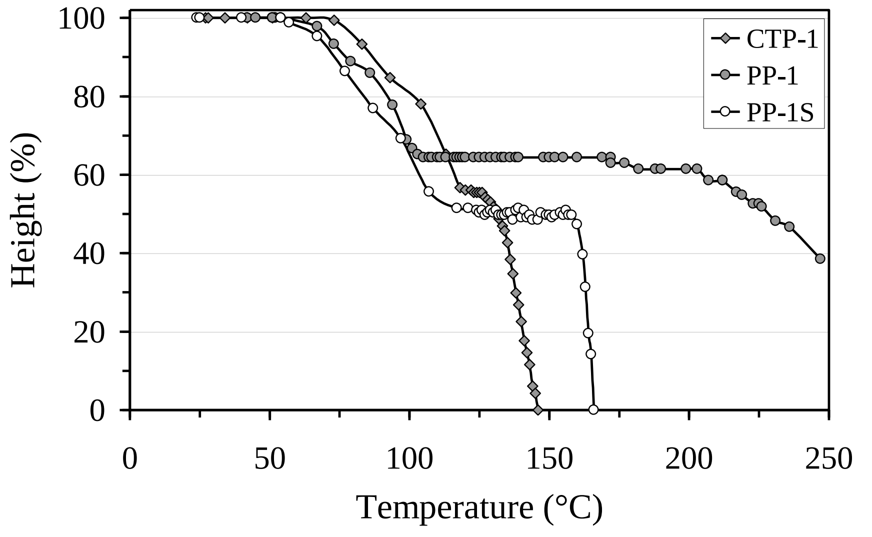

Figure 2. Variation in pitch height with temperature for (a) CTP-1, (b) PP-1 and (c) PP-1S, using calcined petroleum coke as substrate.

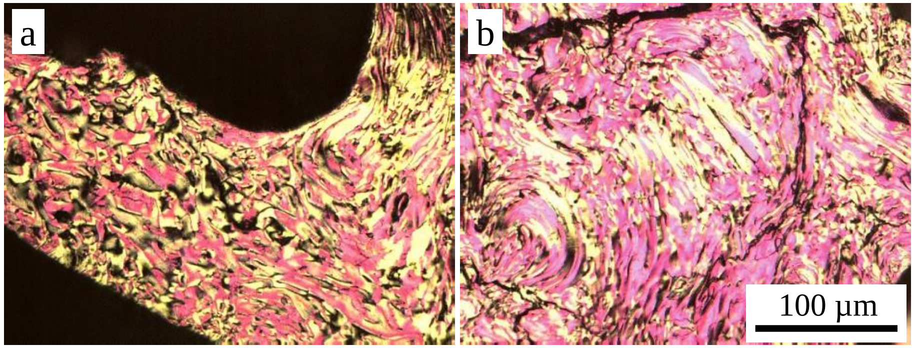

Figure 3. Optical micrographs of cokes obtained from (a) PP-1 and (b) PP-1S.

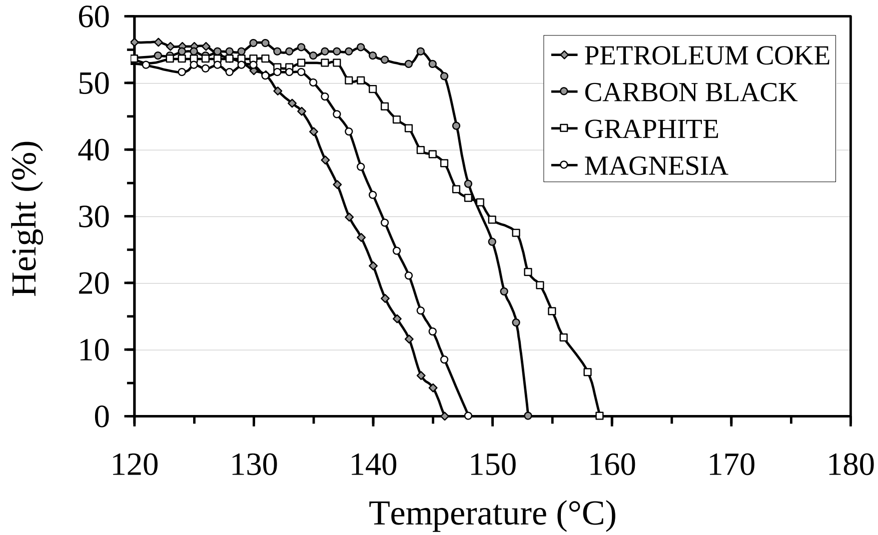

Figure 4. Variation in pitch height with temperature for CTP-1, using petroleum coke, carbon black, graphite and magnesia as substrate.

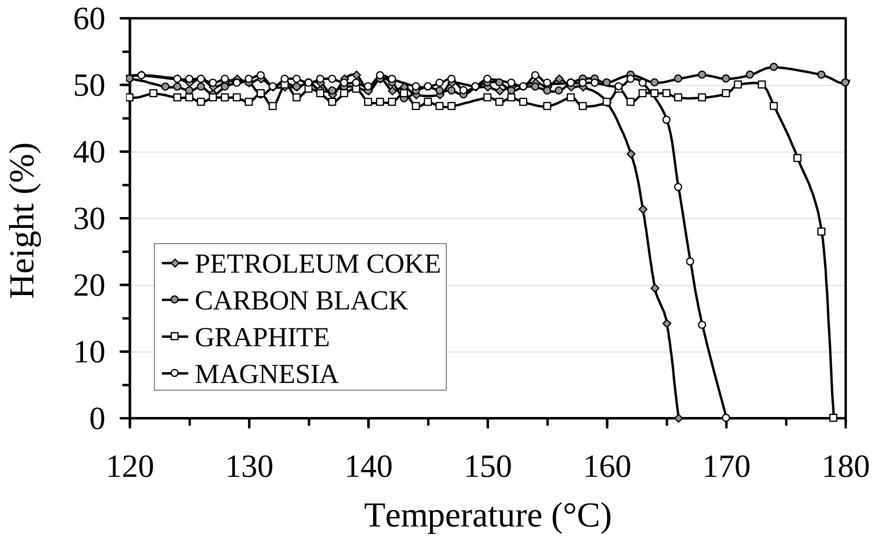

Figure 5. Variation in pitch height with temperature for PP-1S, using petroleum coke, carbon black, graphite and magnesia as substrate.

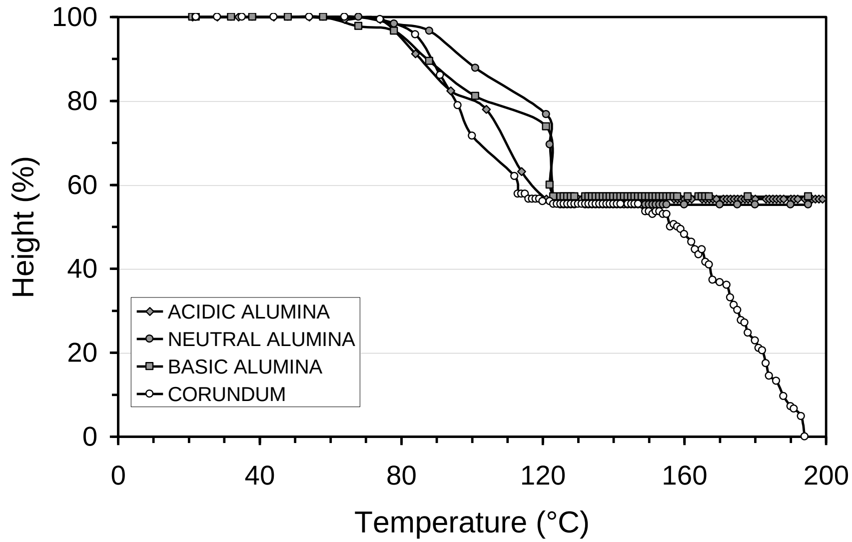

Figure 6. Variation in pitch height with temperature for CTP-1 and PP-1S, using crystalized alumina (corundum) as substrate.

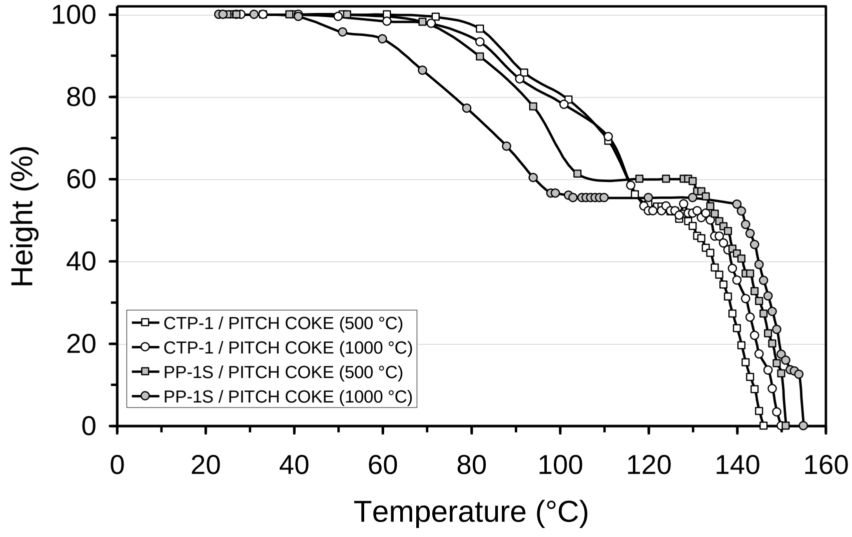

Figure 7. Variation in pitch height with temperature for CTP-1 and PP-1S, using pitch coke obtained at 500 and 1000 °C as substrate.