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RESEARCH ARTICLE

Extraction of Coal-tar Pitch by Supercritical Carbon Dioxide. Dependence of Chemical Composition of the Extracts on Temperature, Pressure and Extraction Time

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Abstract

Several extractions of coal-tar pitch were performed using supercritical fluid carbon dioxide. The relationships between extraction yield during supercritical fluid extraction (SFE) and the variables temperature, pressure and extraction time were investigated. For qualitative and quantitative identification of organic compounds, gas chromatography and gas chromatography–mass spectrometry were used. Each SFE experiment was performed at a specific pressure and temperature; the maximum yield was obtained at 200 bar and 125 °C. In general, the yields of all compounds studied increased with increasing temperature, and reached their maximum values at 125 °C; above this temperature, yields remained almost constant. Higher yields were also obtained with greater retention times or higher pressures. Partial selectivity could be achieved by extracting at different constant temperatures and constant pressures.

1. Introduction

Tar is a black, viscous liquid, formed by condensation of gaseous products when using dry distillation. Pitch, the material that remains after the distillation of creosote, is an important precursor of carbon-based materials. The chemical composition of tar depends less on the nature of the material treated than on the conditions under which the dry distillation is performed, particularly the temperature. The main components of the coal-tar pitches are polycyclic aromatic hydrocarbons (PAHs) and their heterocyclic analogues. Some topologically related hydrogenated and alkylated PAHs, carbazolic and pyrrolic N-heterocycles, O- and S-heterocycles and some oligomeric structures have also been found in appreciable amounts in coal-tar pitches.[1] Certain components of coal-tars and coal-tar pitches (particularly PAHs) are widely considered to be environmental pollutants, *i.e.*, mutagens and/or carcinogens.[2] For this reason, much effort has been spent on qualitative and quantitative analysis of tars and pitches.[3-6] Gas chromatography (GC) is usually employed in this research field, since it has proved to be one of the most sensitive techniques for the identification and quantification of PAHs and related compounds.

The chemical analysis of coal-tar related compounds is usually preceded by extraction from the sample matrix. In recent years, supercritical fluid extraction (SFE) has become an important method for analytical-scale extraction. The fact that the values of significant properties of supercritical fluids (SFs) such as density, diffusivity, viscosity, *etc.*, lie between those of liquids and gases is used to explore the advantages of more expeditious and efficient extractions.[7]

It is well known that the quality of supercritical fluid extractions is highly dependent on the conditions under which a particular extraction is performed, especially on the temperature and pressure applied.[8] Owing to decreasing density, the solvent power of a supercritical fluid should decrease with increasing temperature. On the other hand, the solubility of extracted compounds increases with increasing temperature, and gives rise to varying effects of the previous factor on the extraction process.[8] The density of a supercritical fluid increases with increasing pressure, thus enhancing its solvent power.[8] Supercritical fluid pressure thus plays a significant role in extraction selectivity. The influence of pressure on selectivity has been examined by exhaustive supercritical fluid extractions of PAHs retained on deactivated glass.[9] It was shown, by varying pressure at constant temperatures, that material of progressively higher molar mass was extracted with the higher density extraction fluid, enabling selective extractions at various solvating powers. Some overlap of the components occurred in the different fractions, and quantification of the sample components was not performed.

The aim of the present work was to determine optimal conditions for supercritical fluid extractions of a tar pitch, and to study the dependence of the chemical composition (both qualitative and quantitative) of the extracts on temperature, pressure and extraction time.

2. Experimental

The samples utilized in this investigation included the coal-tar pitch N^o 60/65 RB, which is a product from the coke ovens of Suprachem. Carbon dioxide and helium gases were purchased from Air Products, Kempton Park, RSA.

2.1. Supercritical fluid extraction

Supercritical fluid extractions were performed using an ISCO syringe pump, model 100DX (ISCO, Lincoln, NE, USA). The instrument was equipped with a controller, model SFX^{TM} 200, and a restrictor, both manufactured by ISCO. The supercritical fluid used was SFE grade carbon dioxide (99.995% purity). The extractions were performed by means of a 5 cm^3 extraction cell (50 mm x 11 mm internal diameter, Keystone Scientific, Bellefonte, PA, USA), within the ranges of temperature and pressure of 34–165 °C and 80–400 bar, respectively, at a flow rate of 1 cm^3 min^{-1}. In all experiments 0.2 g of the coal-pitch was extracted. The extractions were carried out by collecting five fractions. Extracted samples were collected in 10 cm^3 of methanol in vials that were cooled with a mixture of ice and sodium chloride to avoid the loss of volatile compounds. Solvent was then removed by evaporation under vacuum at room temperature. After the dry samples had been measured, they were dissolved in dichloromethane and submitted for chemical analysis.

2.2. Gas chromatography and gas chromatography-mass spectrometry

Gas chromatography was used for qualitative and quantitative characterization of organic compounds (8610C gas chromatograph manufactured by SRI Instruments, Torrance, CA, USA). The components of the extracted mixtures were identified using a reference standard solution (Restek Corporation, Bellefonte, PA, USA), and the analyses were supported by gas chromatography–mass spectrometry using the Saturn 2000 GC–MS/MS (Varian, Walnut Creek, USA), run in GC–MS mode.

The gas chromatograph was equipped with a MXT-5 capillary column (30 m × 0.53 mm internal diameter), coated with 5% diphenyl/95% dimethyl polysiloxane stationary phase (df = 0.25 μm; Restek Corporation, Bellefonte, PA, USA). Helium (99.9995% purity) was used as carrier gas at a pressure of 8 psi. Injection was on-column at 40 ^{o}C. Analyses were performed using the following temperature programme: 40 ^{o}C for 5 min , heating rates: 10 ^{o}C min^{-1} up to 70 ^{o}C, and then 4 ^{o}C min^{-1} up to 290 ^{o}C, the final temperature being held for 5 min. Detector temperature was 340 ^{o}C. A flame ionization detector was used. For data acquisition and processing, PeakSimple Chromatography Data Systems for GC and LC, Version 1.88, were utilized.

The gas chromatograph–mass spectrometer was fitted with a capillary column (J&W Scientific, Folsom, CA, USA), coated with 5% phenyl/95% dimethylsilicone (25 m × 0.25 mm internal diameter, df = 0.25 μm). Helium at 12 psi head pressure was used as carrier gas. The column flow of the carrier gas was 1.5 cm^{3} min^{-1}. Split mode was used with a ratio of 10:1. The transfer line was kept at 280 ^{o}C, and the injection temperature was 300 ^{o}C. The temperature programme commenced at 30 ^{o}C, held for 5 min, then increased to 270 ^{o}C at 5 ^{o}C min^{-1}. Detection was done by operating the mass spectrometer in the total ion current (TIC) mode, scanning from 30 to 400 u, with a total scan time (including inter-scan delay) of 800 ms. Conventional electron impact (EI) ionization was used with target voltage 5000 V and emission current 10 μA. The ion source was kept at 280 ^{o}C. Data acquisition and processing were performed with Saturn 2000, Version 5.

3. Results and Discussion

3.1. Optimal conditions for supercritical fluid extractions experiments

The first phase was the determination of optimal conditions for SFE experiments. For this purpose the dependence of extraction yield on temperature (T) and pressure (P) was investigated.

In order to determine the dependence of yield on pressure, SFE experiments were performed at a constant temperature of 50 ^{o}C, under pressures of 80, 120, 160, 200, 240, 280, 320 and 400 bar. The extraction yield increased with increasing pressure (apparently due to increasing density) up to approximately 200 bar. With further increasing pressure the yield remained relatively constant (22–23% of original sample mass).

A subsequent series of SFE experiments was performed at a constant pressure of 200 bar at temperatures of 34, 50, 72, 92, 110, 125, 140 and 165 °C. As shown in Fig. 1, the extraction yield increased with increasing temperature up to 125 °C, and remained relatively constant above this value. One can conclude that, at lower temperatures, the effect of enhancing solubility is stronger than that of decreasing solvent density, causing the increasing yield. At temperatures above 125 °C these two opposing effects become balanced, keeping the yield more or less constant.

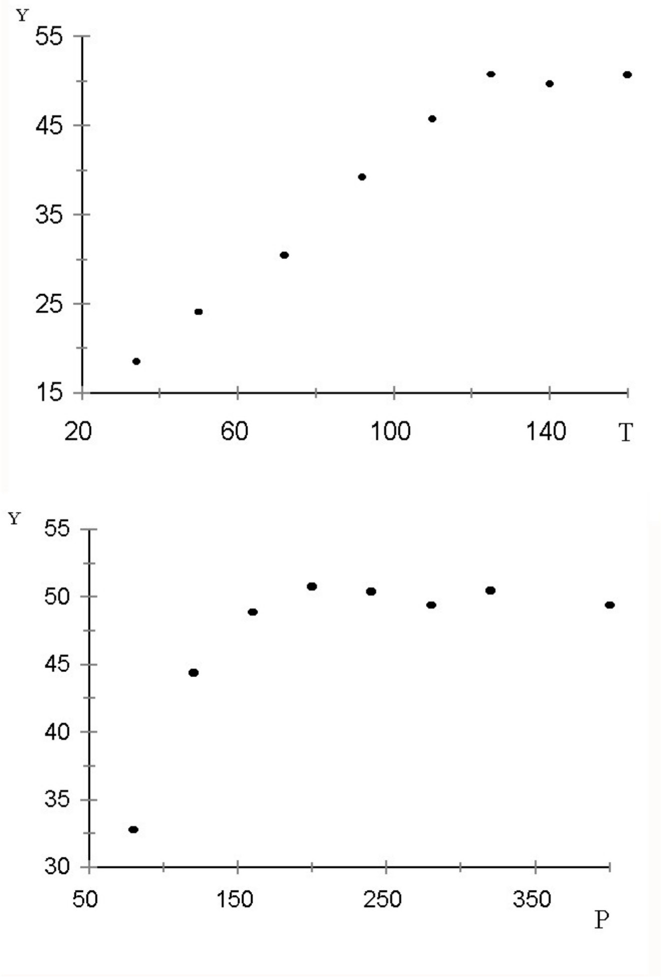
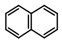
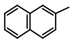
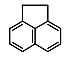
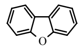
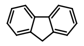
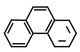
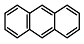
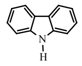
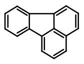
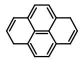
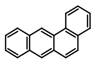
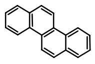


Figure 1 Dependence of yield of extraction on temperature (top) and pressure (bottom). Y, T and P denote yield of extraction (% of the original sample mass), temperature (°C), and pressure (bar), respectively. The same notation is used in Figs. 2 and 3.

The dependence of yield on pressure was then reinvestigated at the optimum temperature of 125 °C (Fig. 1). This graph revealed a trend similar to that shown at

50 °C. The maximum yield was accomplished at about 200 bar, but the yield was now significantly higher (about 50% of the original sample mass), for the reasons explained above.

Table 1 The compounds detected in the coal-tar pitch with yields greater than 0.8% of the original sample mass. RT denotes retention time.

No	Compound		RT	Yield
1		Naphthalene	16.77	5.5
2		2-Methylnaphthalene	20.39	1.0
3		Acenaphthene	26.4	1.4
4		Dibenzofuran	27.36	1.7
5		Fluorene	29.33	2.4
6		Phenanthrene	34.81	7.2
7		Anthracene	35.04	1.7
8		Carbazole	36.3	0.9
9		Fluoranthene	41.74	4.4
10		Pyrene	42.91	3.6
11		Benzo[*a*]anthracene	50.13	1.2
12		Chrysene	50.34	1.6

The results of an SFE experiment carried out under a pressure of 200 bar at 125 °C and flow rate of 1 $cm^3 min^{-1}$ are presented here. The extraction was performed by collecting five fractions: after 15 min of statical extraction the first fraction of 50 cm^3 was collected, whereas the further four fractions contained 40 cm^3. The dried extracted fractions amounted to 41.1, 5.2, 2.4, 1.3 and 0.8% of the original sample mass (in total 50.8%). The components detected with yields greater than 0.8% of the original sample mass are presented in Table 1. In addition, the following minor components were also identified: toluene, phenol, indene, methylphenol (two isomers), dimethylphenol (two isomers), benzothiophene (one isomer), quinoline, ethylmethylphenol (one isomer), indole, methylquinoline (one isomer), 1-methylnaphthalene, biphenyl, ethylnaphthalene (one isomer), dimethylnaphthalene (four isomers), acenaphthylene, methylbiphenyl (one isomer), methylbenzofuran (two isomers), 9,10-dihydrophenanthrene (or anthracene), methylfluorene (one isomer), dibenzothiophene, methyldibenzothiophene, methylphenanthrene (two isomers), phenylnaphthalene (one isomer) and some branched alkanes (C_7–C_9). Several additional compounds could not be identified.

3.2. Dependence of chemical composition of the extracts on temperature and pressure

The amounts of the components in the extracts were also dependent on the conditions under which a particular extraction was carried out. As mentioned above, the first fraction contains over 80% of the total mass of the extracted substance. Thus, only this fraction was considered. The results for compounds **1**, **2**, **5**, **6**, **7**, **9** and **11** (Table 1) will now be discussed.

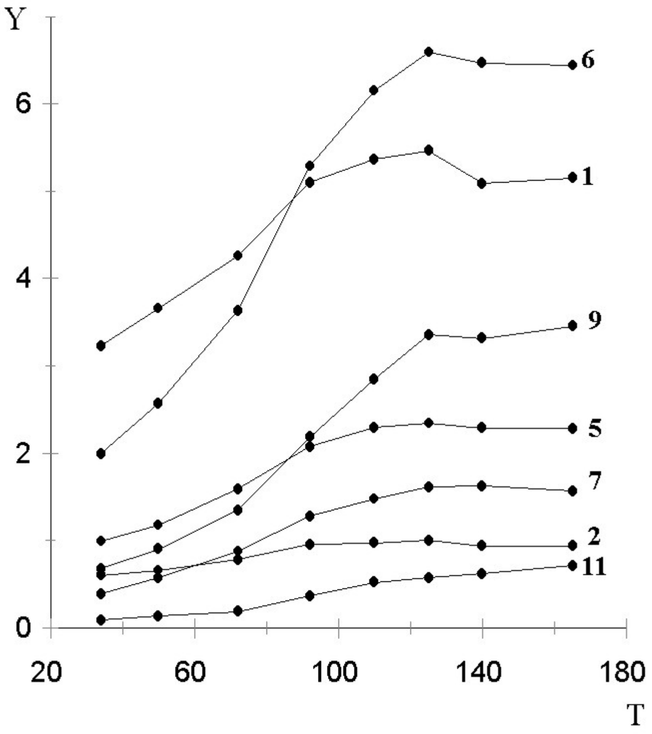


Figure 2 Dependence of the yields of the compounds **1**, **2**, **5**, **6**, **7**, **9** and **11** on temperature. For notation see Fig. 1.

In Fig. 2 the dependences of the yields of these compounds on temperature are presented. All extractions were done at 200 bar. The figure shows that the yields of all compounds increase with increasing temperature, and reach their maximum values at 125 °C. Above this temperature, the yields of the compounds remain almost constant with increasing temperature.

In Fig. 3 the dependences of the yields of the above-mentioned components on pressure are presented. All extractions were done at 125 °C. Each curve starts from a minimum value, passes through a maximum value, and then either decreases or remains more or less constant. The exception is benzo[a]anthracene **11**, for which the yield increases with increasing pressure without reaching the maximum value within the range of pressures used in our experiments. An important feature of the diagram is that different compounds reach their maximum yields at different pressures. For example, the maximum yield of naphthalene **1** is at 120 bar, whereas that of phenanthrene **6** is at 200 bar. By inspecting the graphs and the physico-chemical properties of corresponding compounds, it is evident that the position of the maximum value of a particular curve is determined by the retention time of the compound under question: the longer the retention time, the higher the pressure at which the maximum yield is achieved. The curves of the compounds with short retention times (for instance, those for naphthalene and 2-methylnaphthalene) reached their maximum values at lower pressures before decreasing. The curves representing the components with intermediate retention times (e.g., phenanthrene, anthracene and fluoranthene) reached their maximum values at moderate pressures, and then remained more or less constant with increasing pressure. Finally, the yield of the compound with the longest retention time considered here (entry 11 in Table 1) continuously increased with increasing pressure. One would expect that this curve would also achieve a maximum value, but at a pressure above 400 bar (cf. Fig. 3). Since retention time is directly proportional to molar mass, the observations may be explained as follows: the components of lower molar masses are extracted more efficiently at lower pressures; those with intermediate molar masses reach their maximum yields at moderate pressures; whereas the maximum yields of those with high molar masses are seen at higher pressures.

Curves representing compounds **3**, **4**, **8**, **10** and **12** are not presented in Figs. 2 and 3, but their behaviour is in perfect agreement with that of the compounds with similar retention times. Note that each single SFE was performed under constant pressure and temperature, unlike exhaustive extraction, which involves a change in pressure.[9] Partial selectivity was achieved by extracting at different constant temperatures and constant pressures.

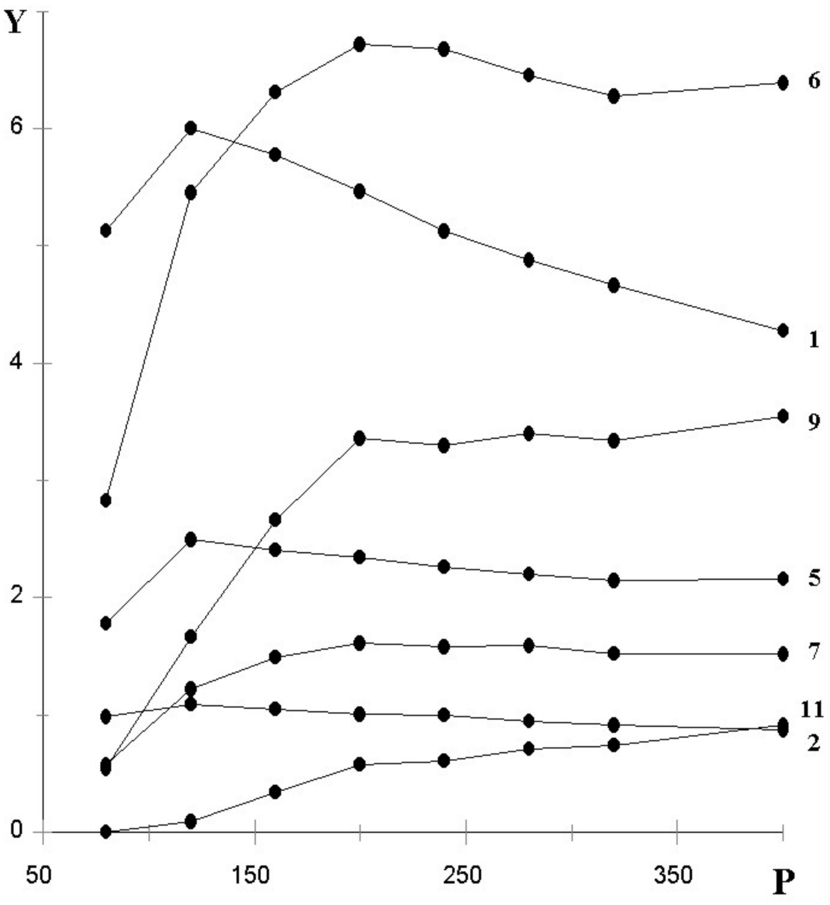


Figure 3 Dependence of the yields of the compounds **1**, **2**, **5**, **6**, **7**, **9** and **11** on pressure. For notation see Fig. 1.

3.3. Dependence of chemical composition of the extracts on time

An SFE experiment was performed with the aim of showing that it was possible to gain higher selectivity by collecting fractions of smaller volumes. Under the optimal conditions of temperature and pressure (125 °C and 200 bar, respectively), 100 cm^3 of the extract was collected in 10 equal fractions over 100 min at a flow rate of 1 cm^3 min^{-1}. Yields and chemical compositions of all fractions were determined, and the dependence of composition of the fractions on time was examined. In Fig. 4 the yields of the components **1**, **2**, **5**, **6**, **7**, **9** and **11** versus time are presented. Note that, in this case, the yield of each component has been calculated as a percentage of the total mass of the corresponding fraction.

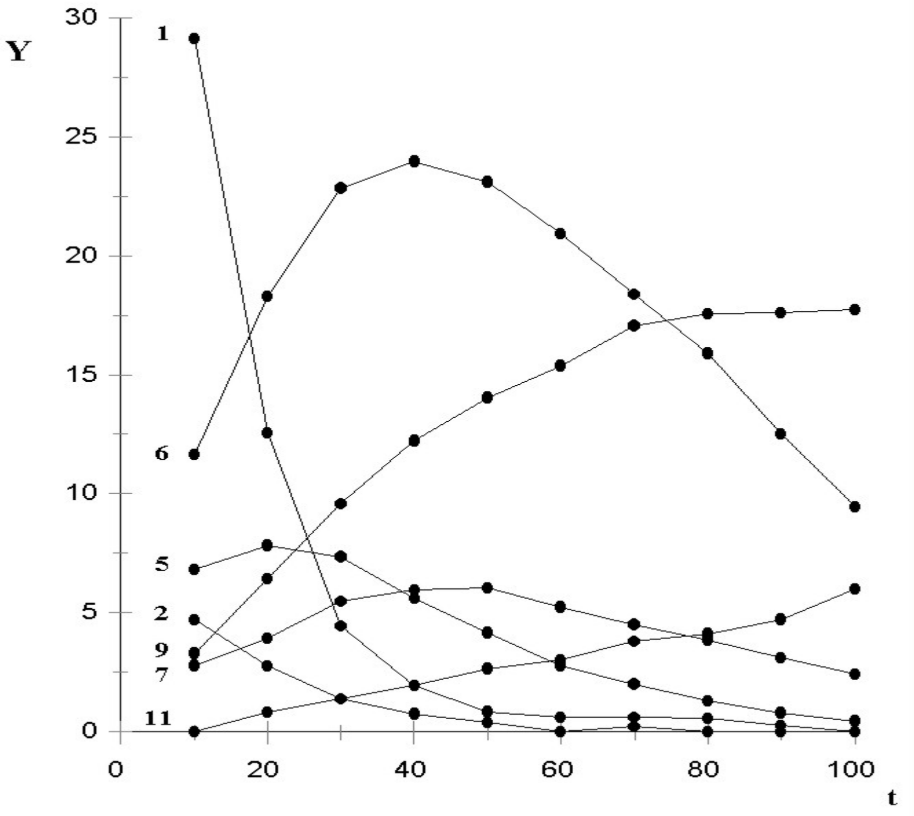


Figure 4 Dependence of the yields of the components **1**, **2**, **5**, **6**, **7**, **9** and **11** on extraction time (t). The yield (Y) of each component is calculated as a percentage of the total mass of the corresponding fraction.

Fig. 4 reveals a trend similar to that shown in Fig. 3: the maximum yields of different compounds are achieved at different time intervals after beginning the extraction. The position of the maximum of a particular curve is determined by the retention time (i.e., molar mass) of the compound in question: the longer the retention time, the longer the extraction time at which the maximum yield is achieved. Thus, in the case of compound **11**, the maximum yield is shifted to longer extraction times. Fig. 4 undoubtedly indicates the fraction in which a particular compound is present as the dominant component. For example, naphthalene, phenanthrene and fluoranthene dominate in the first, fourth and tenth fraction, respectively. On the other hand, the yield of the extraction (calculated in relation to the original sample mass) continuously decreases with the extraction time. Taking this fact into account, it turns out that the amount of, for example, phenanthrene in the first fraction is 2.0% of the original sample mass, whereas, although it is the dominant component in the fourth fraction, its yield is significantly lower (1.1%).

The data produced by our experiments may be utilised in a kinetic study of the extraction process. Concentration–time data, extrapolated from the experiments, may be used to calculate the rate constant of extraction for each component. The temperature dependence of the extraction yield and rate can be utilised to determine the activation energies. This can be used as a possible indication of the type of mechanism that is operative on extracting coal-tar pitch components with supercritical fluid carbon dioxide. A kinetic study is currently being undertaken, as well as mathematical modelling of the extraction process.

4. Conclusions

The efficiency of supercritical fluid extractions is largely dependent on the conditions under which a particular extraction is performed, especially on the temperature and pressure applied. The solvent power of a supercritical fluid decreases, whereas the solubility of the solute increases with increasing temperature. The latter effect is stronger at lower temperatures, resulting in a increasing yield. At temperatures above 125 ^{o}C these opposing effects become balanced, keeping the yield more or less constant. The yield of extraction increases with increasing pressure (apparently due to increasing density) up to about 200 bar. With a further increase in pressure the yield remains relatively constant. This means that the maximum yield of supercritical fluid extractions of the pitch used can be achieved at a pressure of 200 bar and at a temperature of 125 ^{o}C.

The best yield of all components present in the pitch was achieved at 125 ^{o}C. As for pressure, different compounds reach their maximum yields at different pressures, depending on the retention time (i.e. molar mass) of the compound in question: the longer the retention time, the higher the pressure at which the maximum yield is achieved. This means that the components of lower molar masses can be extracted more efficiently at lower pressures, and vice versa. The dependence of yield of the extracts components on extraction time is similar: the higher the molar mass of a certain compound, the longer the extraction time at which its maximum yield is achieved. The fraction in which a particular component is present with the highest concentration can be clearly distinguished. Although each single supercritical fluid extraction was carried out at constant pressure levels and temperature (unlike exhaustive extraction, which involves a change in pressure), partial selectivity was achieved.

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