

Extraction of tar from Turkish coals of various ranks by pyrolysis and application of solvent extraction method for carbon fiber production

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Abstract: Carbon fibers with their high performance are critically important materials for various industries. Coal-based isotropic and mesophase pitches, despite their smaller market share of 10%, can be good alternative to polyacrylonitrile (PAN) based carbon fiber particularly for premium markets such as aviation and defense industry where extraordinary properties like high thermal conductivity and Young modulus are required. Pitch-based carbon fiber production is a complicated process including raw material pretreatment, pitch preparation, melt-spinning, stabilization, carbonization, and graphitization. Each step has a significant influence on the properties and performance of the final carbon fiber product, and thus should be controlled effectively for preparing carbon fiber with desirable performance. In this study, a pyrolysis study has been undertaken on eight Turkish coals of different ranks from lignite to bituminous coals with ash contents varying from 7.25 to 49.20%. The coals have been pyrolyzed at 850 °C for two hours under nitrogen atmosphere in the absence of oxygen during which the emission of released gases of H₂, CO₂, CO and CH₄ in situ measured. The amounts of char, tar and gas have been recorded for each coal. The results based on tar recoveries and aromatic groups as inferred from FTIR spectra were evaluated to find a suitable precursor for use in carbon fiber production. Kırakdere lignite/sub-bituminous coal were selected and subjected to solvent extraction with tetraline at 400 °C temperature and 100 bar pressure to determine the potential of this particular coal for carbon fiber development.

Keywords: carbon fiber, coal, tar, pitch, pyrolysis

1. Introduction

Carbon fiber (fiber) is a next-generation fibrous material containing at least 92% carbon in its structure, possessing low density, biocompatibility, superior mechanical properties, and thermal and electrical conductivity. Fibers containing more than 99% carbon are called graphitized fibers or graphite fibers. Carbon fibers, consisting of carbon atoms arranged in a hexagonal structure, are produced by the thermal and chemical decomposition of various organic fiber precursors.

The strong bonding between carbon atoms gives the fiber high tensile strength (Keboletse et al., 2021). Moreover, due to its compositional advantage, it is even lighter than aluminium. Although carbon fiber has only 20% of the density of steel, it exhibits a tensile strength 10 times higher than steel. For this reason, it is a preferred material in sports equipment, the automobile industry, wind turbines, medical devices, and especially aerospace and aviation, which require high mechanical strength and lightness (Choi et al., 2019).

Due to its high strength, lightness, and ergonomics, the global carbon fiber market has approached 200,000 tons/year, and this amount is expected to triple in the next 10 years. Among the most popular precursor materials, polyacrylonitrile (PAN) fibers account for 90% of the carbon fiber market. In recent years, the share and importance of coal/petroleum-based mesophase pitch is increasing; fossil-based carbon fibers due to their lower production cost and superior electrical and thermal properties

compared to polymeric PAN-based ones, their use in more technological fields such as the defence industry has given serious momentum to coal-based carbon fiber production.

Petroleum- and coal-based mesophases are prepared by catalytic thermal or direct thermal (non-catalytic) methods (Otani, 1965). Thermal catalytic methods are less preferred because of many disadvantages (Shi and Ma, 2019). Direct thermal methods have continued to be used since the late 1990s. The formation of a carbonaceous mesophase ideally consists of PAHs with a molecular weight between 300 and 1200 Daltons (AMU). Numerous studies have shown that free radical reactions in coal pitch can change the content of macromolecules, the size of PAHs, the content of aliphatic or heteroatom-containing functional groups, and the stacking degrees of condensed PAHs in the mesophase (Apicella et al., 2017; Cho et al., 2021; Kim et al., 2016; Niu et al., 2021; Yang et al., 2016).

In recent years, studies on coal or petroleum pitch using the Supercritical Carbon Dioxide Extraction Process (SCE) or solvent-based extraction processes using hydrogen or nitrogen gases have been tested at low temperatures (300-400 °C) and pressures of 50-200 bar (Hill et al., 2022a; Hill et al., 2022b; Thompson et al., 2024). For a proper fiber spinning process, these short-chain aromatic compounds must be removed, and the average aromatic molecular weight needs to be adjusted to the range of 300-1200. In this case, the isotropic pitch obtained by separating low-molecular-weight compounds in the first stage is converted into predominantly polycyclic aromatic structures (PAH) ranging from 300-1200 AMU through heat treatment in the 350-450 °C range.

Currently, coal tar (CT) or coal tar pitch (CTP) is mainly produced as a by-product of the metallurgical coking process; however, this process remains limited by stricter environmental regulations due to the cost of high-quality coals and shrinking market demand. In this case, relatively abundant low-rank coals could be a cheaper source to reduce CT/CTP production costs. However, due to the chemical nature of low-rank coal tar, CT/CTP produced by pyrolysis, gasification, or metallurgical coking processes needs further refining, as it cannot meet the mesophase (MP) criteria. Especially since general properties such as low tar yield (about 5-10% by weight) and lower carbon content, higher ash and oxygen content are not suitable for MP pitch feedstock, methods of liquefying coal with a solvent or carbon dioxide under temperature and pressure to convert coal into liquid fuel are receiving more interest instead (Wang et al., 2023a). In this way, the organic part of the coal can be separated from inorganic ash-forming substances. Subsequent liquefaction reactions trigger hydrogenation reactions by adjusting the temperature (300-450 °C) and pressure (up to 300 bar), facilitating the production of desired chemical products by converting approximately 40-95% of the raw coal by weight (Hutchenson et al., 1991).

While the solution spinning technique is normally used in carbon fiber production processes involving PAN polymer, the melt spinning fiber production technique is generally preferred in the coal-based mesophase pitch process. After the wire drawing, the precursor fiber is oxidized in air under mild pressure at 200-300 °C to ensure molecular alignment, rendering it thermoset. The resulting relatively stable fiber is finally carbonized at approximately 1500 °C in an inert atmosphere to obtain the final carbon fiber.

It should be clarified that the two techniques differ fundamentally. In solution spinning, the PAN precursor is dissolved in a solvent, and the fiber is formed by coagulation of the polymer solution; this route is used because PAN degrades before melting. In melt spinning, by contrast, the coal- or petroleum-based mesophase pitch is heated above its softening point and extruded directly as a molten fiber, which makes the process solvent-free and better suited to the thermoplastic nature of pitch (Edie and Mchugh, 1999).

In this study, pyrolysis of eight different types of Turkish coals, from lignite to hard coal, was carried out at 850 °C under a nitrogen atmosphere, and the emissions of H₂, CO₂, CO, and CH₄ gases formed were measured in situ in order to find a suitable coal sample for CF production. FTIR technique was used to select the most suitable coal sample for further purification by solvent extraction techniques to obtain a precursor for carbon fiber spinning.

2. Materials and methods

2.1. Materials

Seven coal samples and one asphaltite sample of different characteristics and coalification degrees from various regions of Türkiye were prepared for analysis by reducing their size using sample reduction methods. Table 1 presents the proximate analysis results for these samples on a dry basis.

Table 1. Proximate analysis results of coal and asphaltite samples used in experimental studies on a dry basis

Coal	Moisture As received (%)	Ash (%)	Volatile Matter (%)	Fixed C (%)	S (%)	Calorific Value (kcal/kg)
Kozlu	3.1	12.38	25.55	62.07	0.21	7305
Kısrakdere	11.4	7.25	44.88	47.87	2.23	6321
Çan	21.6	21.61	41.07	37.32	7.68	5192
Tunçbilek	12.7	45.41	32.85	21.74	3.81	3406
Keles	32.1	22.10	48.03	29.87	3.22	4602
İmbat	15.9	40.78	39.20	20.02	0.73	3127
Beypazarı	29.0	41.77	39.39	18.84	3.19	3562
Silopi	1.2	49.22	32.76	18.02	5.34	3616

Note: Fixed carbon was calculated by difference (Fixed C = 100 – Ash – Volatile Matter, on a dry basis)

As shown in Table 1, the % ash content of these samples ranged from 7 to 49, and their calorific values ranged from 3600 to 7300 kcal/kg. While preparing samples for pyrolysis experiments, the samples were prepared as much as possible free from very fine sizes ($-3.36+0.420$ mm) in order to increase the reaction rate with small size but also to prevent the entrainment of powders due to the nitrogen gas given to the reactor. To avoid deviation from the original coal sample due to sample losses, size reduction processes were carried out with sieve control. The samples were oven-dried for at least 2 h at 105 °C to remove about 10% moisture. The effect of moisture on the extraction efficiency was not investigated as a separate variable because, in our set-up, the release of water vapour interfered with the measurements; the samples were therefore dried until the moisture was removed before pyrolysis.

2.2. Methods

2.2.1. Pyrolysis experiments

Despite realizing rank differences on tar production, pyrolysis experiments were carried out on eight Turkish coals at 850 °C in order to treat them under the same reference state. Nitrogen gas was fed to the reactor at a flow rate of 1 dm³/min throughout the pyrolysis to prevent undesired oxidation reactions during the experiments. The nitrogen gas flow rate also determines the residence time of the formed pyrolysis vapors in the reactor. Similarly, for effective heat transfer, based on experience gained from previous experimental studies, the reactor rotation speed was selected as 5 rpm.

This study deliberately selected a reference pyrolysis temperature of 850 °C. The primary objective was not to maximise the tar (liquid) yield, for which a lower window of about 450–600 °C is optimum, but rather to compare all eight coals under a single, severe reference state and to promote the formation of a highly aromatic, low-H/C tar suitable as a pitch-type precursor for carbon fiber. At elevated temperature the primary tar undergoes secondary cracking and aromatisation, which raises the relative content of condensed polycyclic aromatic structures desirable for mesophase development, while the in-situ evolution of H₂, CH₄, CO and CO₂ provide a sensitive fingerprint of each coal's pyrolytic reactivity. Although coking of bituminous coals is typically done at 900–1100 °C, the temperature of 850 °C was selected because the majority of our coals is of low-rank type and thus requires lower pyrolysis temperature to get more tar fraction as recommended by Keboletse et al., 2021 and He et al., 2021.

Each experiment was carried out for approximately 3 hours until the pyrolysis gas exit from the reactor ceased; this is just to make sure that the process is complete in such a semi-pilot set up. Solid and liquid pyrolysis product yields were determined by weighing the solid residue (char) remaining in the reactor at the end of the experiment and the liquid pyrolysis products collected in the liquid traps at the reactor exit. The gas product yield was calculated by subtracting the amount of collected solid and liquid products from the amount of coal initially loaded into the reactor. The composition of the pyrolysis gas was followed by taking instantaneous gas measurements throughout the pyrolysis reaction.

All of the experimental studies were carried out in the existing semi-pilot scale batch pyrolysis system at the ITU Synthetic Fuels and Chemicals Technology Center. Fig. 1 shows the block diagram of the pyrolysis unit. The coal content loaded into the cylindrical flanged tube reactor is continuously

stirred by blades built on a rotating shaft. The rotation speed of the shaft, set to 5 rpm, was adjusted remotely with a control program. A continuous nitrogen/water vapor/carbon dioxide gas feed line to the reactor allows the pyrolysis reaction to take place under inert or reactive gas atmospheres. The temperature of the reactor is controlled by thermocouples from inside the furnace and from the outer surface of the reactor.

The system includes a wax/oil catcher, a cooling column, and an open spray-type washing column. After the pyrolysis gas is freed from pyrolysis oil and wax compounds, it is sampled online by the syngas analyzer (MRU SWG 200) connected to the gas line of the pyrolysis unit. All gas products are safely discharged to the atmosphere by burning in an afterburner. At the end of the tests, the reactor is cooled to ambient temperature in a nitrogen gas atmosphere. Then, char is removed from the reactor and weighed for mass-balance calculations. Wax, pyrolysis oil, and aqueous products are collected in traps and containers under the cooler and washing columns, respectively. Gas yield is calculated by subtracting the collected char and wax/liquid products from the weight of the raw material pyrolyzed for that particular experiment.

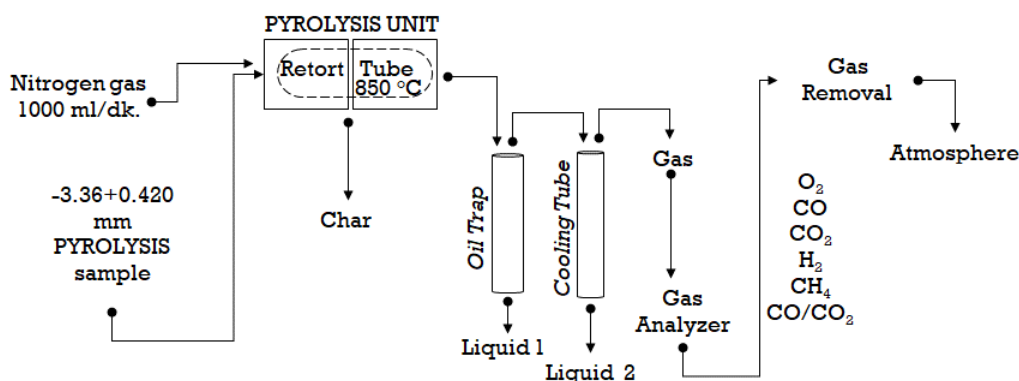


Fig. 1. Block diagram of the batch pyrolysis experimental unit

2.2.2. Solvent extraction experiments

Solvent extraction experiments were performed in a reactor using -3.36+0.420 mm Kırakdere coal at a constant pressure and a ratio of 100 g coal to 200 cm³ solvent (Tetraline), depending on the temperature. In each experiment, coal and solvent were manually charged into a 1-dm³ reactor. Then a small amount of CO₂ (approximately 5 bar) was introduced into the system to purge all channels of oxygen. After entering the target temperature and pressure values on the touch control panel, the start button was pressed, and the temperature began to rise, reaching the set value (for example, 400 °C) in approximately 60 min. Meanwhile, due to the autogenous pressure of the solvent, the pressure increased as the temperature rose; the resulting pressure-temperature profiles could be monitored both from the control panel and remotely. Once the temperature reached the set point, if the pressure was lower than the set value, CO₂ was supplied until it reached 100 bar, followed by a 1-hour soaking (cooking) time to allow the coal and solvent to react at that specific temperature. At the end of the experiment, the reactor was opened, and after filtering, the tar and the char were weighed. Subsequently, the tar that had penetrated into the char was extracted using a Soxhlet extractor. The tar obtained from the extraction and the tar obtained after the Soxhlet extraction were combined and weighed, and their amounts were recorded to calculate the coal conversion and liquefaction yields. Samples taken from each product were stored for analysis. CO₂ was used for three distinct purposes at different stages of the experiment: (i) an initial ~5 bar charge to purge oxygen from the system before heating; (ii) as an inert pressurising medium, supplied only if the autogenous pressure fell short of the 100 bar set-point; and (iii) after the 1-hour soaking period, CO₂ was fed at 50 cm³/min during a separate sweeping step to transfer the liquefied products from the reactor into the Sep 1 and Sep 2 separators for collection of the tar. CO₂ was therefore not fed continuously during the soaking (cooking) stage itself; the 50 cm³/min feed rate reported in the caption of Fig. 8 refers specifically to this post-sweeping step.

In the solvent extraction (liquefaction) of coal with tetralin, tetralin acts as a hydrogen-donor solvent, and a hydrogen (H₂) atmosphere is generally preferred to enhance the transfer of active hydrogen to

the coal-derived radicals, thereby suppressing retrogressive (re-polymerisation) reactions. Although an external hydrogen (H_2) atmosphere is reported to enhance this hydrogen-transfer effect further and improve tar quality, CO_2 was deliberately selected as the process gas at the present stage of this study for safety reasons; the use of an external H_2 atmosphere is planned in future.

3. Results and discussion

3.1. Pyrolysis product yields and gas emissions

The experimental conditions and results of the high-temperature pyrolysis study carried out on eight different Turkish coals are given separately below in Tables and Figs. H_2 , CH_4 , CO_2 , and CO gas emissions observed as a function of time during the pyrolysis process are given in Figs. 3-6, respectively. As shown in Table 2, pyrolysis of Çan lignite yielded 59.7% char, 20.2% pyrolysis oil, and 20.1% pyrolysis gas. The high char yield is attributed to the high ash content of Çan coal, which contains approximately 20.61% ash on a dry basis. Çan lignite is presented first as a representative, detailed example of three-stage lignite pyrolysis behavior; the same reasoning and gas-evolution framework are then applied to the remaining coals in the following sub-sections.

Table 2. Comparative pyrolysis products of various coal samples pyrolyzed at (850 °C)

Product	Çan	Kozlu	Silopi	Keles	Kısrakdere	Beyazarı	Tunçbilek	İmbat
Char	59.7	73.7	69.6	41.4	59	55.2	71.5	65.8
Tar	20.2	5.9	5.2	36.2	17.6	20.7	13.3	12.3
Gas	20.1	20.4	25.2	22.5	23.4	24.1	15.3	21.9
Hydrogen Amount*, m ³	0.215	0.360	0.055	0.209	0.287	0.139	0.155	0.050

* Total volume of released hydrogen gas (m³), integrated over the whole pyrolysis run; the gas concentrations in Figs. 2-5 are instantaneous values (%)

In high-temperature pyrolysis of Çan lignite, carbon dioxide, methane, and carbon monoxide are formed first. As pyrolysis progresses, hydrogen gas (Fig. 2) is released at its maximum production rate. Along with hydrogen, the carbon monoxide concentration also increases. Lignite pyrolysis can be evaluated in three stages; in the first stage, free and chemically bound water loss occurs. In this stage, volatile organic compounds also thermally decompose, with the dehydration of organic components occurring partially. The content of volatile matter together with fixed carbon determines the yield of tar, oil, and coke. High volatile content will result in coal yielding large amounts of oil and tar. Coals considered good for coking contain volatile matter ranging from 15% to 45% (Keboletse et al., 2021; Kim et al., 2016). The carbon content of the coal and the volatile matter ratio to the sum of the oxygen and sulfur contents (VM/(O+S)) were found to be predictor variables that determined the extraction yield (Lino et al., 1988). Extraction yield versus nitrogen and sulfur percentage of 8 coal samples yielded no significant correlation (Kim et al., 2016b).

As a result of dehydration, decarboxylation, and decarbonylation reactions, pyrolysis gas rich in H_2O , CO_2 , and CO is formed initially. In this way, a significant part of the oxygen content of the lignite passes into the gas phase (He et al., 2021; Ofoe et al., 2025). Apart from Kozlu bituminous coal exhibiting 0.360 m³ H_2 gas emission, Kısrakdere coal with 0.287 m³ H_2 emission ranks first among all the other coals; using relatively lower-rank coals is an important incentive for efficient operation of carbon fiber production.

CO/CO_2 formation continues through the rearrangement or cleavage of acetyl (CH_3CO-), ether ($C-O-C$), and/or ester ($-COOR$) bonds found in the coal structure. Due to the exothermic nature of decarboxylation reactions, CO_2 formation occurs at lower temperatures compared to decarbonylation reactions, which are endothermic and give CO . For this reason, it is expected that the CO_2 concentration is higher than the CO concentration in the initial stage of the reaction (Zhang et al., 2018; He et al., 2021).

Methane formation in Fig. 3 is associated with the breakdown of methoxyl ($-O-CH_3$), methyl ($-CH_3$), and methylene ($-CH_2-$) groups. It is evaluated that the presence of these structures in the structure of

coal can increase methane formation (Zhang et al., 2018; Ofoe et al., 2025). In addition, methane and hydrogen formation are expected to increase with the thermal breakdown of condensable organic vapors formed during pyrolysis. The high hydrogen concentration observed in the later stage of pyrolysis is evaluated to be a result of this situation (He et al., 2021; Li et al., 2021). Hydrogen and carbon monoxide formation is also an indication of other secondary reactions taking place in the gas phase and under the catalytic effect of char. For example, hydrogen and carbon monoxide are formed as a result of the reaction of char with water vapor, and methane is formed as a result of dealkylation of tar with water vapor (Ahamed et al., 2019).

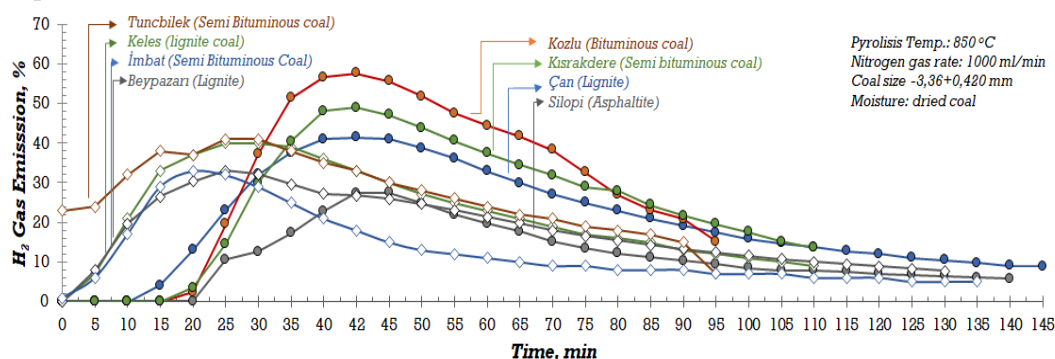


Fig. 2. H₂ gas emissions released in pyrolysis processes carried out on different coals (scaled on total gas amount basis)

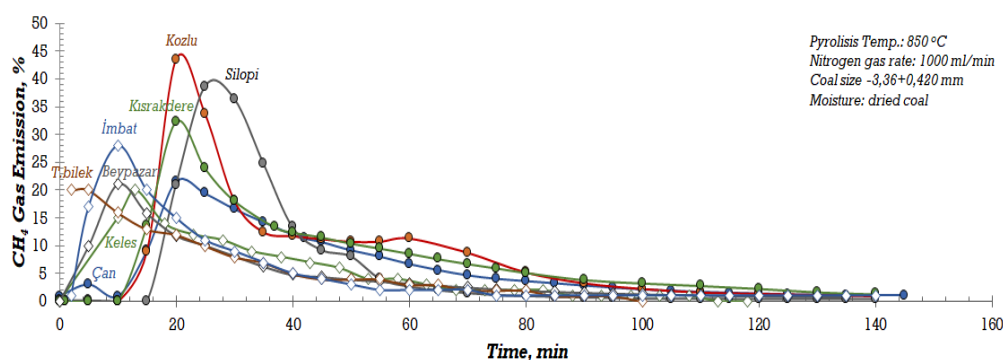


Fig. 3. CH₄ gas emissions released in pyrolysis processes carried out on different coals (scaled on total gas amount basis)

Gas emissions during pyrolysis of Kozlu coal were observed as a function of time. Figs. 2 to 5 show the pyrolysis process carried out on Kozlu coal. When the pyrolysis results of Kozlu coal are examined, the pyrolysis tar product yield is 5.9%. The char yield was 73.74%, and the gas product yield was 20.4% (Table 2). When gas analysis trends were examined, carbon dioxide formation in Fig. 4 was also very limited. This behavior was attributed to the low pyrolysis reactivity of Kozlu coal, which has a bituminous structure (Ofoe et al., 2025). The char formed under the effect of high heat gasifies and turns into carbon monoxide and hydrogen. Dehydration, decarbonylation, and decarboxylation reactions taking place were limited during pyrolysis, and thus liquid product formation was also at a minimum level.

Gas emissions in the pyrolysis process carried out on Silopi Asphaltite were observed as a function of time. Table 2 presents the results for Silopi asphaltite; the pyrolysis product yield of Silopi coal is similar to that of Kozlu coal. Silopi coal pyrolysis yielded 69.60% char, 5.20% pyrolysis oil, and 25.20% gas product. Although a similar product yield profile to Kozlu coal was obtained, it exhibited a different behavior compared to Kozlu coal when the gas composition was examined. High methane formation draws attention as a result of the pyrolysis of Silopi coal; this result may occur as a result of the bond breaking of the polymeric tar content and/or methoxyl (-O-CH₃), methyl (-CH₃), and methylene (-CH₂) groups of Silopi coal. It is envisaged that Kozlu and Silopi coals could give different product distributions if the pyrolysis temperature is lowered.

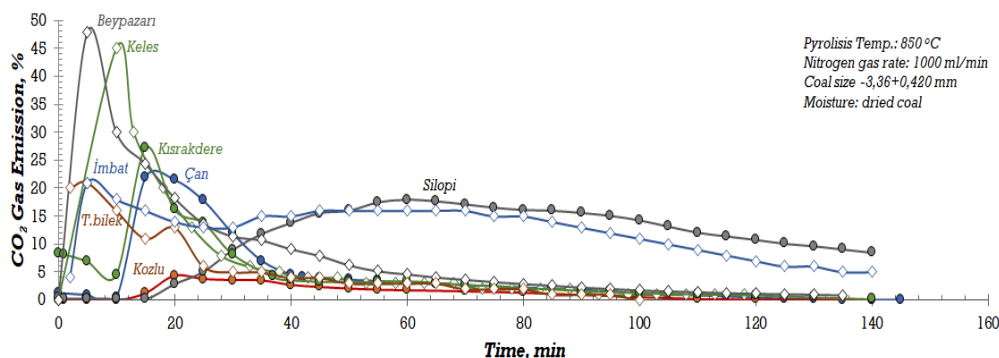


Fig. 4. CO₂ gas emissions released in pyrolysis processes carried out on different coals (scaled on total gas amount basis)

A quite high tar product yield of 36.2% (Table 2) was obtained on pyrolysis of Keles coal at a temperature of 850 °C. The gas product yield was 22.5%, and it showed similar behavior to other coal samples tested. A liquid product with a low H/C ratio and a more aromatic structure may have been obtained at a high carbonization degree at 850 °C. Hydrogenation reactions may be decisive in the characteristics of the pyrolysis liquid hydrogen formed as a result of secondary pyrolysis reactions. Furthermore, more aromatic formation can be expected through the reaction of furanic compounds with light olefins via Diels-Alder and subsequent dehydration reactions. These reactions offer clues that can help predict the liquid product characteristics of the pyrolysis gas composition. Methane and hydrogen formation trends as a result of Keles pyrolysis point to the presence of similar reactions.

The pyrolysis process carried out on Kırakdere coal gas emissions was observed over time, as shown in Fig. 2. The pyrolysis product yield of Kırakdere coal shows 59.0% char, 17.6% pyrolysis oil, and 23.4% pyrolysis gas. Gas composition trends and concentration changes are quite similar to the results obtained with Keles coal. However, 50% less pyrolysis oil yield was obtained compared to Keles coal, which may be a result of Kırakdere coal having a similar pyrolysis reactivity to Keles coal but having less volatile matter content.

Table 2 shows Beypazari coal gas emissions as a function of time during the Pyrolysis process carried out on Beypazari coal. The pyrolysis results for Beypazari coal and Kırakdere coal are quite similar. While 55.2% char, 20.7% pyrolysis oil, and 24.1% pyrolysis gas yield were obtained with Beypazari coal, these values were recorded as 59%, 17.6%, and 23.4%, respectively, with Kırakdere coal. The observation of a quite severe carbon dioxide peak in the first stage of pyrolysis with Beypazari coal points to the presence of carboxylic groups in Beypazari coal. An increase in the carboxylic group concentration of coal is a measure of the coal being more reactive pyrolytically. Since decarboxylation reactions are exothermic, a spontaneous temperature increase in the reactor is expected due to the exothermic reaction heat. This situation acts positively in terms of pyrolysis kinetics. Thus, Beypazari coal can be pyrolyzed at a lower temperature with higher yield than Kırakdere coal.

Gas emissions observed as a function of time for the Pyrolysis of Tunçbilek Coal are given in Figs. 3-6. A very high char yield of 71.5% char, 13.3% pyrolysis oil, and 15.3% pyrolysis gas was observed as a result of pyrolysis at 850 °C. When the pyrolysis gas formation trend was examined, a carbon dioxide peak was not observed, and a formation trend with a quite wide and low percentage concentration was obtained for carbon dioxide. Low carbon dioxide formation shows that the pyrolysis reactivity of Tunçbilek coal is low. Hydrogen, carbon monoxide, and methane formation as an indicator of the char gasification reaction draws attention. The ash of Tunçbilek coal is around 40-45% on a dry basis, and thus high char yield originates from the high ash content of Tunçbilek coal. Pyrolysis oil yield also remained low as a result of the 28-30% volatile matter content of Tunçbilek coal on a dry basis.

Table 2 shows gas emissions as a function of time during the pyrolysis of İmbat coal. The pyrolysis of İmbat coal yields 65.8% char, 12.3% pyrolysis oil, and 21.9% gas. A high amount of carbon monoxide formation (Fig. 5) draws attention in İmbat coal. Carbon monoxide is formed as a result of endothermic carbonylation and secondary pyrolysis reactions. Decarbonylation reaction is a primary pyrolysis reaction and is also a measure of the oxygen content of coal. As the oxygen content of coal increases, pyrolysis oil with a higher oxygen content is obtained, which oligomerizes more easily (Ofuo et al.,

2025). In addition, the presence of organic acids makes the pyrolysis oil quite corrosive; the oxygen content of the pyrolysis oil of İmbat pyrolysis will be high.

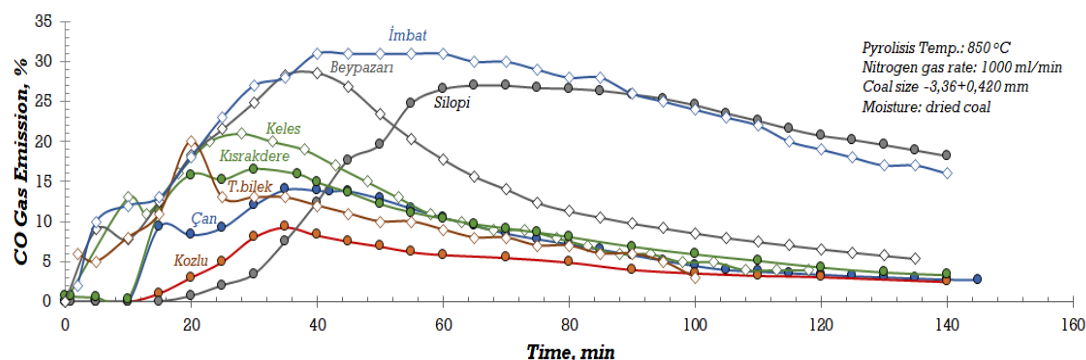


Fig. 5. CO gas emissions released in pyrolysis processes carried out on different coals (scaled on total gas amount basis)

3.2. Comparative analysis of gas emission trends

When hydrogen gas formation trends are compared (Fig. 2), it is seen that the highest hydrogen concentration was reached with Kozlu coal. Hydrogen formation trends obtained for Kozlu, Kırakdere, Çan coals, and Silopi asphaltite are quite similar to each other, and maximum hydrogen concentrations are 58%, 49%, 42%, and 28%, respectively. Pyrolysis oil yields for these coals were recorded as 5.9%, 17.6%, 20.2%, and 5.2%, respectively. A change was observed in this ranking only for Silopi asphaltite. In contrast, the Silopi sample showed a very high methane concentration. This situation occurred because Silopi asphaltite has a different structure from the other three coals (Sezer et al., 2008).

When methane formation trends are examined (Fig. 3), the highest methane concentrations were obtained for Kozlu, Silopi, Kırakdere, and İmbat coals. Methane concentrations of 44%, 39%, 33%, and 28% were reached for these coals, respectively. While methane formation was observed in the first stage of pyrolysis for İmbat, Beypazarı, Keles, and Tunçbilek coals, methane formation increased in the later stage of pyrolysis for other coals (Zhang et al., 2018). 12.3%, 20.7%, 36.2%, and 13.3% pyrolysis oil were obtained for İmbat, Beypazarı, Keles, and Tunçbilek coals. There appears to be no direct relationship between methane formation and pyrolysis oil yield.

When carbon dioxide concentrations (Fig. 4) are examined, the initial carbon dioxide formation of Beypazarı and Keles coals is the highest. Around 45-50% carbon dioxide formation was observed initially for both coals, and it is evaluated that these coals are quite reactive. Pyrolysis oil yields for Beypazarı and Keles coals are 20.7% and 36.2%, and coal reactivity appears to be a decisive factor in pyrolysis oil yield (He et al., 2021).

When carbon monoxide formation trends are examined (Fig. 5), the highest concentrations occur between 25-30% for İmbat, Silopi, and Beypazarı coals. Kozlu coal showed the lowest carbon dioxide and carbon monoxide concentrations. This situation indicates that the reactivity of Kozlu coal is extremely low. Kozlu coal produced an extremely low pyrolysis oil yield of 5.9%. The low pyrolysis yield observed for Kozlu coal may have resulted from insufficient concentrations of carboxyl and carbonyl surface groups (Ofoe et al., 2025).

Because the ash contents of the coal and asphaltite samples (Apak et al., 2002) used in pyrolysis studies are different from each other, in order to better understand the effect of changes occurring only from the organic structure on pyrolysis products and especially gas emission concentrations, pyrolysis product distributions were recalculated on a dry ash-free basis and given in Table 3; it shows that the highest liquid yields were obtained in the pyrolysis of Keles (46.47%) and Beypazarı (35.55%) coals.

3.3. FTIR studies on various coals

Eight different grades of coals were subjected to pyrolysis at 850 °C. The pyrolytic tars were dissolved in Tetrahydrofuran (THF) and the FTIR spectra of insoluble fraction (THF-Ins.) are presented in Fig. 6. The most appropriate coal was selected in order to delineate its suitability for further carbon fiber

studies. A review of the literature on this subject (Cooke et al., 1986; Guillen et al., 1992; Wang et al., 2023b; Zhang et al., 2023; Alcañiz-Monge, 2001; Zhou et al., 2014; Niu et al., 2017) have directed us to focus on Kırakdere coal for the following reasons.

Table 3. Pyrolysis product distributions obtained as a result of pyrolysis processes (dry ash-free basis)

Coal	Ash (%)	Char (%)	Tar (%)	Gas (%)
Kozlu	12.38	69.98	6.73	23.28
Silopi	49.22	40.13	10.24	49.63
Kırakdere	7.25	55.80	18.98	25.23
İmbat	40.78	42.25	20.77	36.98
Tunçbilek	45.41	47.61	24.36	28.03
Çan	21.61	48.59	25.77	25.64
Beypazarı	41.77	23.06	35.55	41.39
Keles	22.1	24.65	46.47	28.88

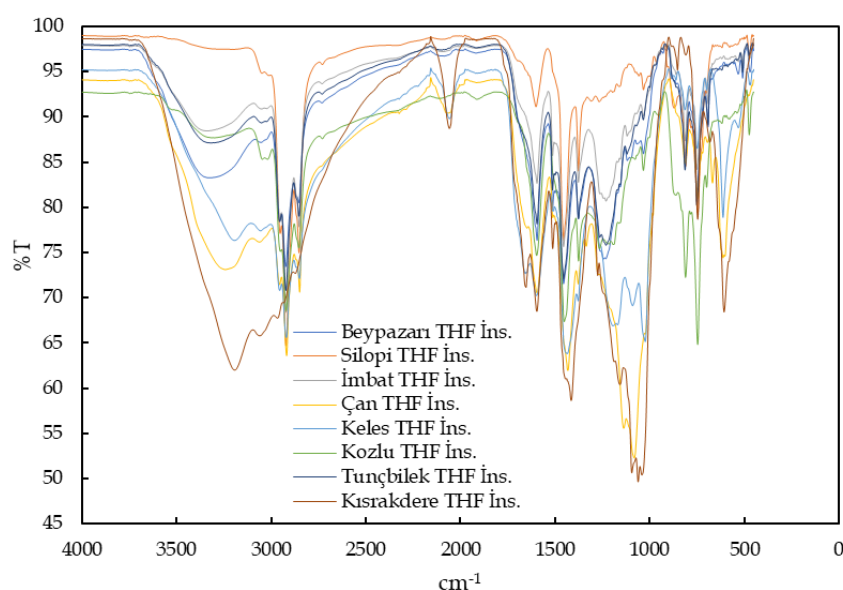


Fig. 6. FTIR spectra of THF-insoluble fraction of tars whose coals were pyrolyzed at 850 °C

Among all samples, the Kırakdere sample shown in Fig. 6 exhibited the most distinct IR spectrum. The main difference was that aromatic peaks were more dominant than aliphatic peaks, indicating a higher aromatic character in this sample. Another notable feature was the relatively low intensity of peaks corresponding to substituted aromatic hydrogen and adjacent aromatic hydrogen vibrations, suggesting that the aromatic structures in this sample contained fewer substituted groups compared to the other samples.

Although the vibration peaks corresponding to aliphatic and aromatic groups were not very distinct in the raw Kırakdere coal sample, they became much more pronounced for Tar and THF Ins – products (Wang et al., 2023b). The aromatic C-H stretching bands of both samples appeared as intense broad peaks at 3180 and 3070 cm^{-1} . Broad hydroxyl-bond peaks corresponding to hydrogen-bonded -OH structures were also observed in the 3350-3250 cm^{-1} region.

Aliphatic Carbon Balance at 2920-2850 cm^{-1} exhibits more pronounced (deeper) asymmetric and symmetric C-H stretching peaks in this region, indicating that alkyl side chains and aliphatic bridges (such as methylene bridges) are still preserved within the structure. This is highly typical for a high-quality lignite such as Kırakdere lignite/subbituminous coal (Ibarra et al., 1996).

In both tar and THF Ins. samples, aliphatic C-H stretching bands were less dominant and were observed in the 2945-2850 cm^{-1} region. Both samples exhibited absorption bands in the 1600-1400 cm^{-1}

region due to aromatic hydrocarbon $\text{C}=\text{C}$ - stretching vibrations. Another notable peak was the $\text{C}=\text{O}$ absorption peak observed around 1650 cm^{-1} . C-heteroatom (O or N) stretching peaks appeared as a broad band between 1250 and 1190 cm^{-1} . Low-intensity peaks corresponding to substituted aromatic hydrogen and adjacent aromatic hydrogen vibrations were observed at 850 , 775 , and 750 cm^{-1} for both samples.

Oxygenated Groups and Hydrogen Bonds at $3600\text{--}3200\text{ cm}^{-1}$ in the OH stretching region, the peak depth of Kırakdere is at a moderate level. Due to its nature as a high-quality lignite, it is evident that it does not carry the excessive carboxylic/phenolic oxygen load seen in lower-quality lignites, indicating that moisture and heteroatom removal have been successfully achieved. The presence of peaks of aromatic C-H out-of-plane bending at $900\text{--}700\text{ cm}^{-1}$ region indicates that there are available hydrogens ready for substitution around the polycyclic aromatic rings (Fig. 7).

Based on these qualitative interpretations, Kırakdere coal was selected for the preliminary extraction studies due to its high carbon content, low ash content, relatively high aromatic component content, and because, despite being classified as lignite, its characteristics place it within the semi-bituminous coal category.

Kırakdere was chosen over higher tar-yield coals such as Keles and Beypazarı because carbon fiber depends not on how much tar a coal yields but on how well that tar forms a spinnable pitch. Kırakdere has the lowest ash (7.25%), an aromatic, carbon-rich character, and a narrow molecular-weight range, which make it easier to turn into a spinnable pitch with less purification. Aromaticity index alone is not sufficient for such a selection. Kırakdere qualitatively shows the deepest transmittance drops in the aliphatic region, implying a highly aliphatic nature or higher overall organic matter retention in its THF-insoluble fraction. Research is underway for a quantitative analysis. The high sulfur content of Kırakdere (2.23%) is a drawback but not a decisive one. Its effect depends on the sulfur form: thiophenic sulfur can improve the ordering of the mesophase pitch, while sulfoxides and sulfones hinder it (Guo et al., 2025). Moreover, much of the sulfur leaves as H_2S during pyrolysis, and the rest can be removed from the tar by oxidative desulfurization and solvent extraction down to about 0.1%, which is low enough for a mesophase precursor (Fujimoto et al., 1986; Jin et al., 2011).

When these three FTIR spectra shown in Fig. 7 are analyzed together, they reveal the molecular transformations and key structural changes in the Kırakdere sample throughout the pyrolysis and extraction processes for carbon fiber precursor production. The similarity between the tar-phase spectrum and that of the THF-insoluble phase indicates that the molecular weight distribution of the tar obtained from Kırakdere coal is not very broad and contains components with similar structures. This suggests that homogenizing the material to obtain a "spinnable pitch" for carbon fiber production will be easier.

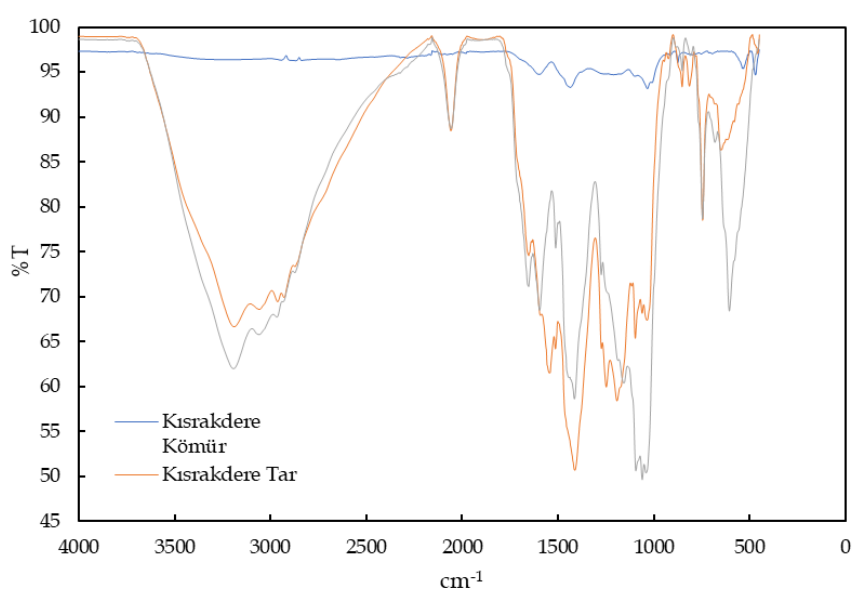


Fig. 7. FTIR spectra of tar obtained by pyrolysis of Kırakdere coal at $850\text{ }^{\circ}\text{C}$, the original coal, and the THF-insoluble fraction obtained by distillation of this tar with THF

3.4. Solvent extraction and MALDI-TOF analysis of Kırakdere coal

Accordingly, we have carried out a series of experiments in a reactor under pressure in the presence of tetraline as a function of temperature to observe the ability of solvent extraction process to increase the amount of tar. Fig. 8 presents the results, with coal conversion plotted against temperature from 375 to 450 °C. The results suggest that 400 °C and 100 bar pressure, with a solvent/coal ratio of 2/1 and a cooking period of 1 hour, are optimum (Chang et al., 2019).

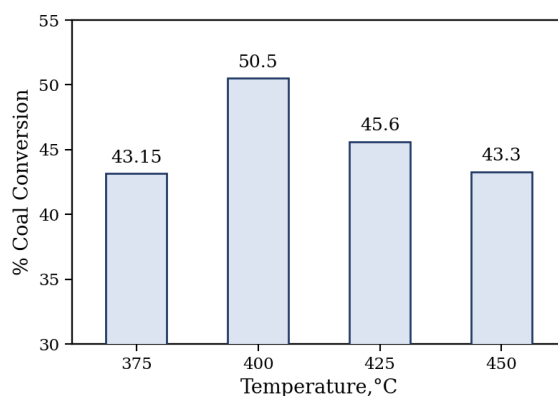


Fig. 8. Extraction of Kırakdere coal with tetraline against temperature at a solvent/coal ratio of 2, 100 bar pressure using 50 ml/min CO₂ gas feed rate for (post-sweeping step) one hour of cooking time

The sample taken at 400 °C was analyzed by MALDI-TOF to find out the molecular weight distribution of the THF-insoluble fraction of the extracted tar. The results are illustrated in Fig. 9 as a function of the segmental distribution of molecular weights of the tar in the range of about 200-1800 AMU. The results demonstrate that the raw tar contains a useful range of molecular weights, possibly PAH compounds, but has to be trimmed both from the upper part of pre-asphaltenes and the lower part of volatile compounds to achieve an ideal MW range of about 300-1000 AMU. This requires either solvent extraction with solvents like toluene before it is sent to melt spinning for carbon fiber production (Zabihi et al., 2019).

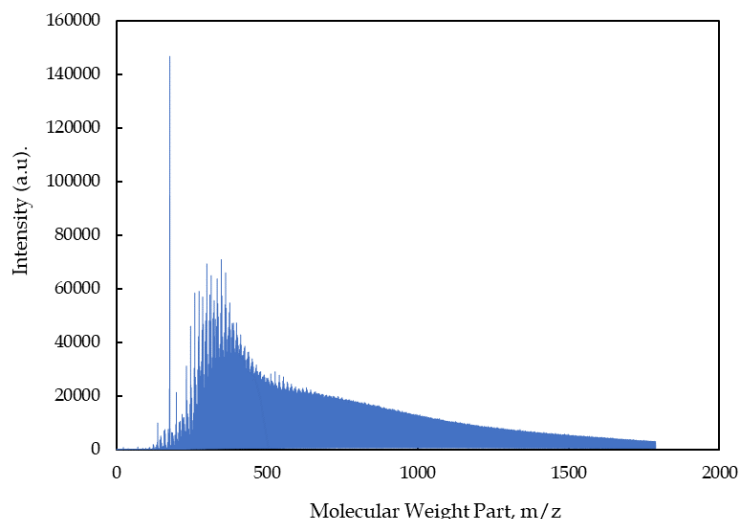


Fig. 9. MALDI-TOF results of Kırakdere THF-Ins. fraction

4. Conclusions

Pyrolysis studies indicated that the initial composition of the coal determines the pyrolysis reactivity of the coal. The oxygen content of the coal originates from carboxyl and carbonyl groups. As the concentration of these groups increases, the pyrolysis kinetics of the coal increases, and the pyrolysis oil yield improves at this rate. Successive hydrogenation processes are needed to reduce the oxygen content of pyrolysis oil to obtain a higher degree of carbonization and lower oxygen content.

Considering the molecular transformation and critical structural changes, FTIR spectra of eight different coals, tars, and their THF-insoluble fractions indicated that the Kırakdere coal sample was suitable for further solvent extraction studies in order to produce a carbon fiber precursor. Accordingly, Kırakdere coal was subjected to solvent extraction tests as a function of temperature in the range of 375-450 °C and 100 bar pressure with CO₂ gas for a period of one hour. An optimum was found at 400 °C, with a coal conversion yield of 50.5%. Molecular weight distribution analysis using MALDI-TOF indicated that the tar MW distribution ranging from 200 to 1800 can be further purified to produce a good precursor for carbon fiber production.

Acknowledgments

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