

Characterization of the mechanism of gasification of a powder river basin coal with a composite catalyst for producing desired syngases and liquids

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ABSTRACT

The objective of this research was to examine the mechanisms of FeCO_3 , Na_2CO_3 , and $\text{FeCO}_3\text{-Na}_2\text{CO}_3$ based catalytic coal gasification of a low-sulfur sub-bituminous Wyodak coal from the Powder River Basin (PRB) of Wyoming. X-ray diffraction (XRD), Mössbauer spectroscopy, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), gas chromatography (GC-MS) and nuclear magnetic resonance spectroscopy (NMR) were used to perform the analyses. Use of composite catalysts for coal gasification overcomes some of the limitations of the standalone use of Na or Fe catalysts. The XRD results are consistent with interactive mechanisms or the formation of Na-Fe oxides as the catalytic pathway. Mössbauer spectroscopy indicated the presence of metallic iron and cementite in the char at different stages. The Fe catalysts were better at tar decomposition than the Na catalysts, as indicated by GC-MS analyses. NMR spectra confirmed that tar compositions vary with the catalytic mechanism. FTIR analysis confirmed the presence of high yields of aromatic components and long aliphatic chains in the tar. Composite Fe-Na catalysts provide a method to tailor the amounts and composition of product generated during gasification.

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1. Introduction

Upcoming strict CO_2 emissions regulations [1–5] by the Environmental Protection Agency (EPA) will no longer be achievable by traditional means of coal combustion. The “Standards of Performance for Greenhouse Gas Emissions from New Stationary Sources: Electrical Generation Units” [6] proposed rule sets limits in the range of $950\text{--}1200\text{ lb}_m\text{ CO}_2/\text{MWh}$ for new stationary combustion turbines depending on the heat input rating. Therefore, increasing dependence on different energy sources has drawn attention to clean coal technologies, such as coal-to-liquids processing, due to its potential for lower environmental impacts and higher efficiencies than direct coal combustion [7]. Coal-to-liquids processing can be achieved through direct coal liquefaction (DCL) or indirect liquefaction (ICL). The core of the ICL process is gasification. Coal

gasification is an energy intensive process that requires high temperatures; however, the use of catalysts is one of the most effective methods to improve its efficiency, reduce the operational temperature, and manipulate the selectivity of the product syngas, which is the feed for ICL. Furthermore, process oriented life-cycle analyses (LCA) of the emissions generated by a 381 MW IGCC unit over a 30 year life of the plant, indicates total emissions of CO_2 on order of $5.34 \times 10^7\text{ Mt}$, whereas at the same conditions, direct coal combustion may generate $\sim 24\%$ more CO_2 compared to gasification without any CO_2 capture technology, and at least 37% when CO_2 capture technologies are in place [8].

Catalysts play a major role in the efficiency enhancement of many industrial chemical processes in the energy and fossil fuel processing industries, including coal utilization and petrochemical processing and refining, in which over 80% of the processes are catalytic. Examples include fluid catalytic cracking, naphtha reforming, isomerization, Fischer–Tropsch synthesis, coal gasification, coal tar hydrogenation, and many others [9–13]. Catalysts are also widely used in the pollution remediation industry, where their

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consumption ranges from automotive exhaust treatment to NO_x reduction from coal-fired furnaces [14,15].

Given the complexity of current chemical processes, single component catalysts cannot satisfy some high performance requirements, such as high activity, selectivity, and stability against deactivation [16]. Recent advances in catalytic technology suggest that composite catalysts not only overcome the disadvantages of their individual components, but also synergize their effects by improving reaction rates more than the sum of their individual components rates [16]. Composite catalysts are widely used in sulfur recovery units, the fuel cell industry, naphtha reforming in petrochemical refining, etc. [13,16,17]. There are many kinds of composite catalysts, including simple physical mixtures, crystallite composites obtained by intergrowth, in situ combinations, matrix materials, host-guest composites, hybrid composites that comprise a matrix material, and hierarchical porous composites [16–18]. Some of the catalytic performance enhancements observed with the use of composite catalysts include support effects, stabilization of active components, formation of new compounds that act as stabilizers, dual-function effects in elementary reactions, adjustment of acid and base properties, redox performance control, surface bonding state control, adsorption/desorption and diffusion enhancement, and improved migration or transference of active species [16,19–21].

Proper use of composite catalysts has great potential in terms of improving the efficiency of many industrial applications. In particular, Na–Fe composite catalysts have demonstrated high effectiveness in applications such as coal combustion, NO_x reduction, and enhancement of carbon conversion rates in coal gasification [15,22]. Traditionally, the process of reducing nitrogen oxides from coal-fired boilers has been accomplished through the use of selective catalytic reduction (SCR), which typically employs NH₃ as a reducing agent in a reactor upstream of electrostatic precipitators and scrubbers. However, recent findings have demonstrated that the addition of Na–Fe composite catalysts to the char prior to combustion inhibits NO emissions [15]. Use of such catalysts could reduce many associated costs and simplify this pollution remediation operation.

Suzuki et al. [22,23] studied the effects of Na–Fe composite catalysts on coal gasification of Yallourn char using NaHFe(CO)₄, while Song and Kim [22,23] investigated the same catalysts by mixing Na₂CO₃ and FeSO₄ and impregnating them onto an Alaskan subbituminous coal. In both cases, a synergistic effect was observed in conversion rates.

Additional applications of sodium–iron (Na–Fe) composite catalysts include the hydrogenation of carbon dioxide and Fischer–Tropsch synthesis. However, in the latter application, the effect of these catalysts has been varied, proving to be negative when residual Na from the material preparation participates in the reaction [10,24,25].

An additional benefit of Na–Fe composite catalysts for coal gasification observed by our research group is the remediation of coal tar. Coal tar has been classified as all volatile organics from coal that condense at room temperature, generally with a molecular weight greater than benzene [26] and is highly undesirable due to the negative process effects associated with its condensation and deposition. Reported tar tolerance limits in gaseous fuels vary widely for different machines: 50–500 mg/m³ for compressors, 50–100 mg/m³ for internal combustion systems, and 5 mg/m³ for direct-fired industrial gas turbines [27]. Without the use of catalysts, significant steam reforming of tars occurs only above 900 °C [24]. Catalytic steam and dry reforming reactions are a promising way to remove the tar components from the syngas at lower temperatures [24]. Other studies have revealed that Fe-based catalytic coal gasification can substantially reduce overall tar yield [28,29] and reduce the proportion of tar acids, though in hematite (Fe₂O₃)

catalyzed coal gasification, a complete tar breakdown still required temperatures above 900 °C [28,30].

Changes in selectivity (H₂ and CO yield augmentation), conversion rate enhancement, activation energy decrease, tar reduction, and general improvements of the overall efficiency of the process are some of the advantages of composite Na–Fe catalysts. These are directly correlated to additional process advantages, such as decreased gasification temperatures with associated increase of the gasifier service life. Further research on these catalysts is crucial to the advancement of carbon gasification technologies [22,23,31]. The mechanism of the Na–Fe couple acting as catalytic agents has not been studied in depth at this point. Our previous study found that the combined catalysts had advantages over the individual sodium or iron catalysts; this synergistic mechanism could include the presence of sodium iron oxides acting as intermediates or final products, increased Fe mobilization, or a combination of these effects [31]. The previous work raised questions about the mechanism that governs Na–Fe interactions with coal and how are they different from the standalone catalytic activity. This current study focused on the answers to these questions and the description of the catalytic products formed in the coal char. Therefore, the main objective of this work was to determine the mechanisms through which Na interacts with Fe to improve the performance of their individual catalytic capabilities.

2. Experiments

2.1. Materials

2.1.1. Catalyst preparation

Iron carbonate was prepared from 10% (w/v) aqueous solutions with equimolar amounts of FeSO₄·7H₂O (99.81% Matheson, Coleman & Bell) and Na₂CO₃ (99.81% FMC Inc.). The resulting precipitate (siderite, or FeCO₃) was filtered, washed with Na carbonate and distilled water, dried at 92 °C, and calcined in air at 250 °C to produce a brown powder. The FeCO₃ was sieved to retain 125 μm particles and stored in air tight, dark colored containers to prevent structural and moisture content changes. Aqueous Na₂CO₃ 10% (w/w) solutions were prepared with Na₂CO₃ (99.81% FMC Inc.).

2.1.2. Catalyst loading

FeCO₃, Na₂CO₃, and FeCO₃–Na₂CO₃ were used as catalysts for coal gasification. The mixtures of pulverized PRB (200 mesh) coal and catalysts were prepared by adding FeCO₃, Na₂CO₃, or FeCO₃–Na₂CO₃ to obtain the following weight ratios of catalyst to dry ash free (DAF) basis coal: 0%–Fe + 4%–Na, 1%–Fe + 3%–Na, 2%–Fe + 2%–Na, 3%–Fe + 1%–Na, and 4%–Fe + 0%–Na. Proper quantities of the Na₂CO₃ solution and/or FeCO₃ were mixed with the coal, slurried with water, and finally dried at 90 °C for 72 h prior to gasification.

2.2. Char and tar collection

The tests were conducted at local atmospheric pressure, about 75 kPa in our laboratory. FeCO₃–Na₂CO₃ catalysts and coal mixtures were pyrolyzed and gasified in N₂ and H₂O–N₂ mixtures. 5.0 g DAF coal were used for each gasification test. Pyrolysis was performed by flowing 4.1 ml/min of N₂ while heating the sample at a constant rate of 20 °C/min to the gasification temperature of 800 °C. The apparatus used for the catalytic coal gasification includes a set of calibrating gases, mass flow controllers, heaters, water pump, packed bed reactor, furnace, tar collection section and gas chromatograph. The tests were conducted at local atmospheric pressure, about 75 kPa in our laboratory. FeCO₃–Na₂CO₃ catalysts and coal mixtures were pyrolyzed and gasified in N₂ and H₂O–N₂ mixtures. 5.0 g DAF coal was used for each gasification test.

Pyrolysis was performed by flowing 4.1 ml/min of N₂ while heating the sample at a constant rate of 20 °C/min to the gasification temperature of 800 °C. Steam gasification was initiated when this temperature was reached. The flow rate of nitrogen was controlled using mass flow controllers (Porter Instruments series 201 with a 4 channel PCIM4 controller). Steam was added by introducing 0.04 g/min H₂O through a high pressure pump (Scientific Systems-Lab Alliance Series 1) and a coil type vaporizer wrapped with heating tape. The installation used heat-traced 1/4" stainless steel tubing, with the temperature monitored using thermocouples. The coal was pyrolyzed and gasified in a 1/2" stainless steel tube reactor in a tubular furnace (Thermolyne 21100), with ceramic wool holding the coal in place. Char collection was performed by extracting samples at four different conditions: (a) after pyrolysis at 400 °C, (b) after pyrolysis at 800 °C, (c) after 10 min of steam gasification at 800 °C, and (d) after 20 min of steam gasification at 800 °C. Additionally, ash samples were collected by completely gasifying the coal and catalyst mixtures.

2.3. Char and tar characterization

The surface area of the coal/catalyst mixtures prior to pyrolysis and gasification were measured using nitrogen physisorption by standard Brunauer–Emmet–Teller (BET) analysis (Micromeritics TriStar 3000 V 6.04 A).

X-ray diffraction (XRD) analyses were performed on the catalyst and coal mixtures on a Rigaku Smartlab X-ray diffraction system. The analyses were conducted using Cu K_α radiation (1.54 Å). The voltage and current used were 40 kV and 40 mA respectively. The range of 2θ measurements was between 10° to 100° with 0.010° steps. A nickel K_β filter was used to eliminate any K_β radiation.

Mössbauer spectra were obtained at 295 K, 80 K, and 4 K using a source of ~30 m Ci of ⁵⁷Fe on a WEB Research Co. model WT302 spectrometer. Coal samples were mixed with sucrose under acetone and placed in a holder backed by Kapton polyimide film tape. The velocity range of the data was ±10 mm/s in 2048 channels, with acquisition times ranging from 12 h to 6 days depending on the Fe content of the sample. Corrections were made to the data to remove the baseline fraction created by the Compton scattering of 122 keV gamma rays by electrons inside the detector.

Fourier transform infrared spectroscopy (FTIR)/attenuated total reflectance (ATR) analyses were performed on a Nicolet Magna 760 FTIR spectrometer (Thermo Scientific). The instrument has a 1064 nm Nd:YVO₄ excitation laser, an XT-KBr beam splitter, a He-Ne laser for sample alignment, a InGaAs detector, and a computer for automated spectra collection and analysis.

Gas chromatography/mass spectroscopy (GC–MS) for coal tars was performed with an Agilent Technology 7890A GC system with a split-splitless injector (model 7863 Autosampler Injector) fitted with a 5957C VLMSD MS system using a capillary column (HP-5MS, 30m × 0.250 mm × 0.25 μm). Gas chromatography was also used to determine the gaseous effluent composition during pyrolysis; the experimental method details are described elsewhere [31].

All NMR samples were prepared in deuterated chloroform (CDCl₃ or chloroform-d). The light tar fractions were collected by bubbling the reactor effluent through 5.0 ml of chloroform-d at 20 °C. Heavy tar produced in each reaction was dissolved in 2.0 ml of chloroform-d. NMR spectra were acquired at 26 °C on a 600 MHz Avance III Bruker NMR spectrometer equipped with a 5 mm broad band (BBO) probe. 1D ¹H spectra were acquired at 600.162 MHz with 64 scans, 3.5 s acquisition time, and 5 s recycle delay. 1D ¹³C spectra were acquired at 150.925 MHz using one-pulse (30° flip angle) with inverse gated ¹H decoupling, 5 s recycle delay and 0.5 s acquisition time. 5120 scans were signal averaged. In order to distinguish primary, secondary, and tertiary carbons, distortionless enhancement by polarization transfer using a 135° tip angle

Table 1

Tar production and carbon distribution during pyrolysis.

Catalyst	Liquid tar produced after pyrolysis (g tar/g coal)	Carbon fraction in liquid tar	Carbon fraction in vapor product during pyrolysis
Raw coal	0.18	0.49	0.51
0%-Fe + 4%-Na	0.21	0.55	0.45
2%-Fe + 2%-Na	0.18	0.52	0.48
4%-Fe + 0%-Na	0.18	0.44	0.56

(DEPT-135) was used, by averaging 2048 per spectra with 0.3 s acquisition times and 3 s recycle delay. ¹³C spectra were referenced to the solvent chloroform peak triplet (at 77.21, 77.00, and 77.79 ppm) that was externally referenced to trimethylsilane (TMS) at 26 °C. ¹H spectra were referenced to the residual chloroform ¹H peak at 7.25 ppm. ¹³C spectra were processed with zero filling and 0.30 exponential line broadening (¹H spectra) or cosine square window function (¹³C spectra) before Fourier transform. Spectra were processed and analyzed using TopSpin 3.2 and MestReNova 6.0.3 software.

3. Results and discussion

3.1. Gaseous products

The initial mass loss during the pyrolysis period was evaluated during our previous research through thermogravimetric analyses (TGA), indicating that it accounted for ~58% of the initial coal mass at 800 °C for all catalysts [31]. The volatiles are primarily gas phase species at room temperature; however, an important fraction of these volatiles is liquids or coal tars comprised of complex mixtures of aliphatic and aromatic compounds. In addition, water from coal usually remains with the tar as a separate phase. An analysis of the distribution of the carbon released during pyrolysis as well as the relative mass of tar is presented in Table 1. Fe-loaded catalysts yielded smaller quantities of tar, with corresponding higher quantities of vapor product that was mostly comprised of carbon monoxide. Thus, more of the carbon from pyrolysis ended up in the gas phase product with the Fe catalyst. The observed values of liquid tar presented in Table 1 include water. A more extensive composition of the syngas, particularly during the gasification stages, is presented elsewhere [31].

3.2. Solid phase

The physical characteristics of the Wyodak Powder River Basin (PRB) coal used for this research, including composition, heating value, proximate, ultimate and elemental analyses, and TGA, are described elsewhere [31,32]. The surface areas of the catalyst and coal mixtures show an interesting trend with increasing iron content: 1.9 m²/g for 0%-Fe + 4%-Na, 3.2 m²/g for 1%-Fe + 3%-Na, 4.1 m²/g for 2%-Fe + 2%-Na, 7.5 m²/g for 3%-Fe + 1%-Na, and 11.6 m²/g for 4%-Fe + 0%-Na. Increasing surface area with increasing Fe loading suggests possible pore blocking by the Na, thereby reducing accessible carbon sites for gasification. As both our earlier research and other previous studies have shown that Na catalysts considerably improve the rate of gasification [22,31,33], the part of the synergy of adding iron simply appears to be the increased surface area for enhancement of the effect of the sodium.

3.2.1. X-ray diffraction (XRD)

The pure Na catalyst followed the expected trend reported previously for Na₂CO₃ [27,31]. The mechanistic pathway has been shown to involve initial conversion of Na₂CO₃ into metallic Na, then formation of Na₂O and possibly Na₂O₂ as proposed for other alkali carbonates, followed by regeneration of the Na₂CO₃ [34–36]. Fig. 1

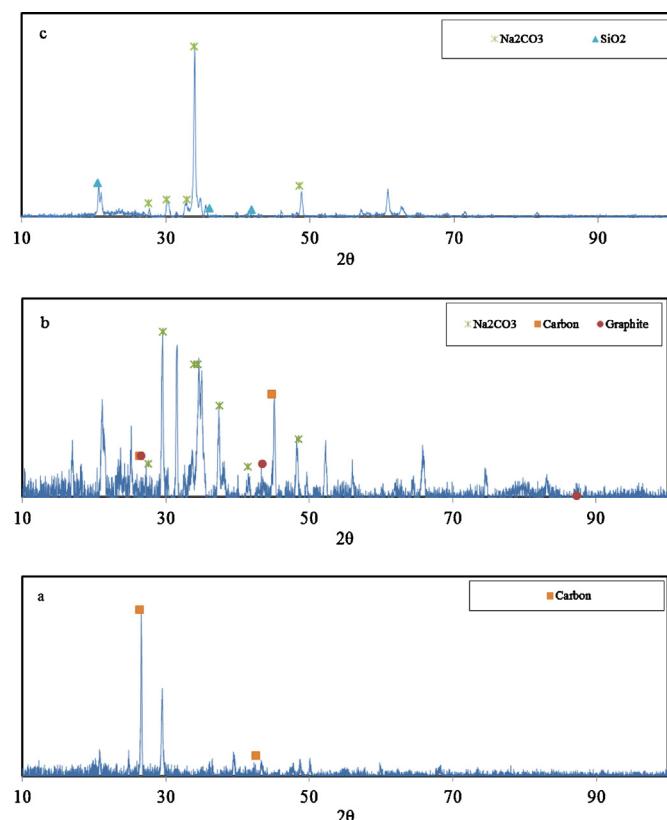


Fig. 1. XRD spectra of 0%-Fe + 4%-Na composite catalyst and coal mixture: (a) at 400 °C pyrolysis, (b) after 20 min of gasification at 800 °C, and (c) ash.

presents the XRD spectra for the 0%-Fe + 4%-Na catalyst and coal mixture at different conditions. Table 2 presents the main peaks in the scanned 2θ range for all the species found in the char and ash samples. In the 400 °C pyrolysis spectrum (Fig. 1a), the main peaks are associated with carbon. The carbon structures appear to change as the reaction proceeds because graphite peaks are visible in the 800 °C gasification spectrum (Fig. 1b). Na_2CO_3 can be observed in the 800 °C gasification and ash spectra (Fig. 1c), indicating its possible catalyst regeneration. Other ash components, such as silicon oxide, are present in the ash spectrum.

The catalytic path for Fe-based coal gasification, particularly involving Fe carbonate, has been proposed to include the following steps [29].



The process includes the conversion of siderite (FeCO_3) into magnetite (Fe_3O_4) and wüstite (FeO), as has been studied in the past [29]. The presence of FeO is also expected at advanced gasification stages and high temperatures, as observed by Popa et al. [29]. The

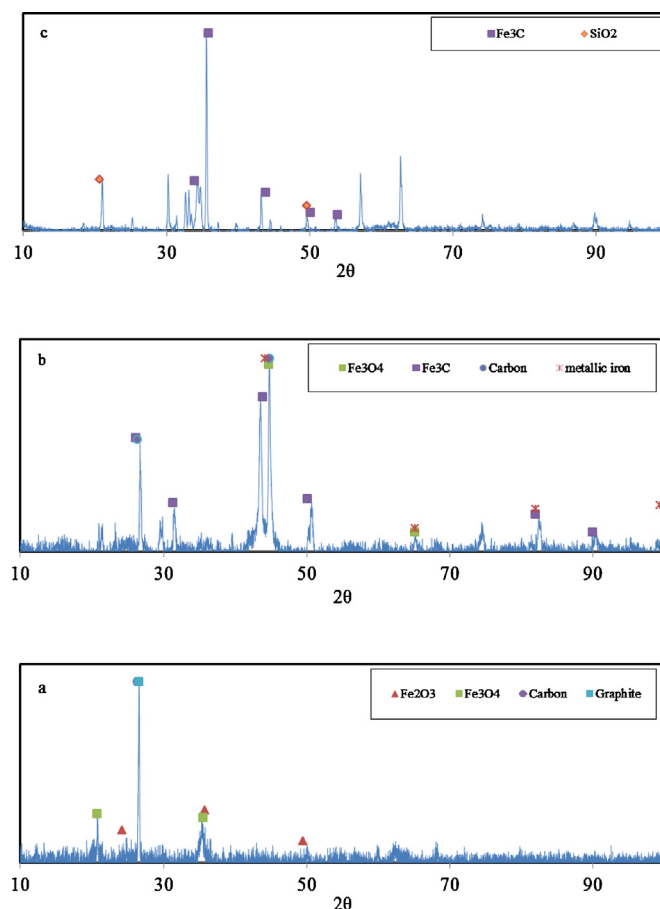


Fig. 2. XRD spectra of 4%-Fe + 0%-Na composite catalyst and coal mixture: (a) at 400 °C pyrolysis, (b) after 20 min of gasification at 800 °C, and (c) ash.

XRD spectra for iron catalyzed reactions (4%-Fe + 0%-Na catalyst) in Fig. 2 at different conditions, indicates the presence of magnetite after pyrolysis at 400 °C (Fig. 2a) and possibly hematite. Following the expected pathway, Fe_3C and metallic iron are observed after 20 min of gasification at 800 °C (Fig. 2b), while only cementite was observed in the ash (Fig. 2c).

Composite catalysts, however, present different behaviors than those of the corresponding individual catalysts. Plausible mechanisms for this process include separate activity of the catalysts, formation of sodium iron oxides, or another synergistic mechanism. In our previous study, the 3%-Fe + 1%-Na composite catalyst presented a much higher conversion potential than that of the 1%-Fe + 3%-Na catalyst, suggesting that high Na with small Fe contents can actually be unfavorable for catalytic gasification; however, Fe-based catalytic gasification decreases the conversion rate at advanced conversion stages, starting between 75% and 89% of the total conversion [29,31]. This limitation is decreased by the presence of smaller amounts of Na in the mixture as the 3:1 Fe to Na catalyst did not show this decrease in the rate at high conversions [31]. A possible explanation for this synergy could be related to the presence of active iron catalytic species once sodium has reached an activity threshold.

The XRD patterns for the 2%-Fe + 2%-Na catalyst at different conditions are presented in Fig. 3. After pyrolysis at 400 °C, the main peaks are associated with magnetite and hematite (Fig. 3a), pointing to the catalytic activity of the iron catalyst. After 20 min of gasification at 800 °C (Fig. 3b), Na_2CO_3 is present, similar to the corresponding 4%-Fe + 0%-Na spectrum (Fig. 2b). Graphite peaks are again present, indicating the structural change of carbon as the

Table 2
XRD main peaks for the present species in char.

Species	Main peaks (2θ)
Carbon	26.34, 43.4, 102.2
Graphite	26.61, 43.45, 87.32
Na_2CO_3	27.6, 29.6, 34, 37.5, 34.5, 48.6
Fe_2O_3	24.16, 35.74, 49.5
Fe_3O_4	20.8, 35.5
Fe_3C	26.18, 31.36, 43.92, 50.07, 82.0
SiO_2	20.61, 49.63, 67.44, 72.84, 74.7
NaFeO_2	21, 30, 44.5

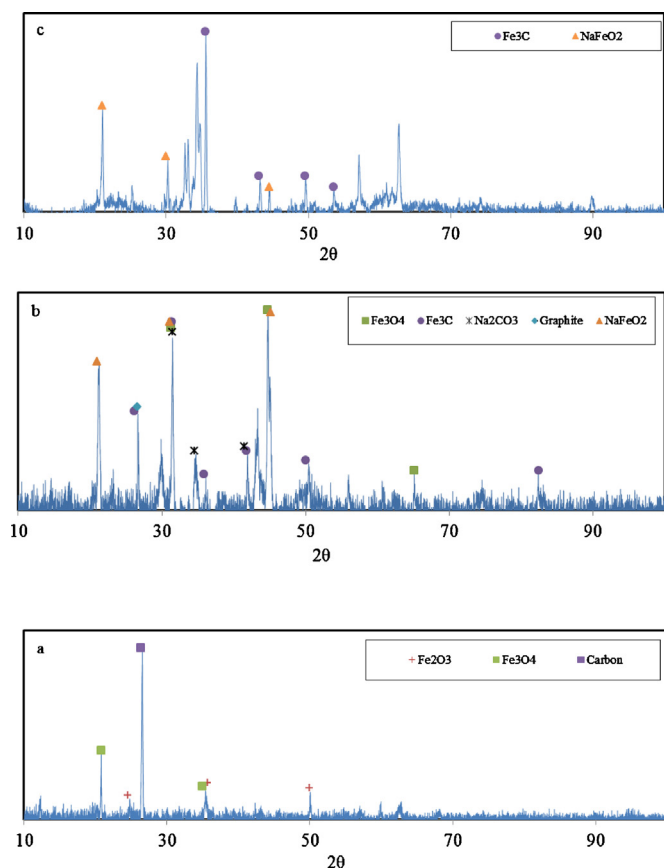
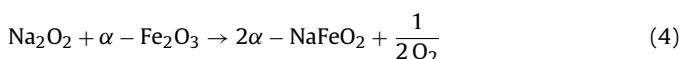
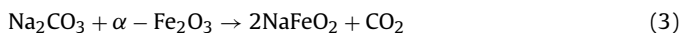


Fig. 3. XRD spectra of 2%-Fe + 2%-Na composite catalyst and mixture: (a) at 400 °C pyrolysis, (b) after 20 min of gasification at 800 °C, and (c) ash.

reaction advances. However, in this spectrum, as well as in the ash spectrum related to the 2%-Fe + 2%-Na catalyst, some of the peaks may be associated with NaFeO₂, which could suggest a possible synergy between these two catalysts. As previously discussed, at an advanced stage of the reaction, i.e. 20 min of gasification (Fig. 3b), the most prominent lines in the diffraction patterns are those for magnetite and natrite (Na₂CO₃), suggesting conversion into the less active Na₂CO₃, although Fe species could still be active. However, the interaction of these species or other iron and sodium oxides, such as hematite, sodium oxide, and sodium peroxide, could still react to form NaFeO₂. The Na–Fe oxide conversion likely occurs when the Fe species are still active on the C surface. The exact mechanism of this reaction is unknown, but Takeda et al. [37] have noted that Na carbonate and hematite, or Na oxide(II) and hematite, have the capability of forming α-NaFeO₂ and β-NaFeO₂, with intermediate phases of Na doped γ-Fe₂O₃. A possible set of reactions to form potential catalysts is provided below [37]



The synergistic effect of this composite catalyst is documented in this analysis and in the results of our previous research, which showed that the rate of steam gasification with this composite catalyst exceeded at most conditions the rate of either pure Fe or Na catalysts. Thus, the composite catalysts have greater effects on the rate of steam gasification than the sum of their individual contributions. Suzuki et al. demonstrated this enhancement using NaHFe(CO)₄ for coal gasification [22].

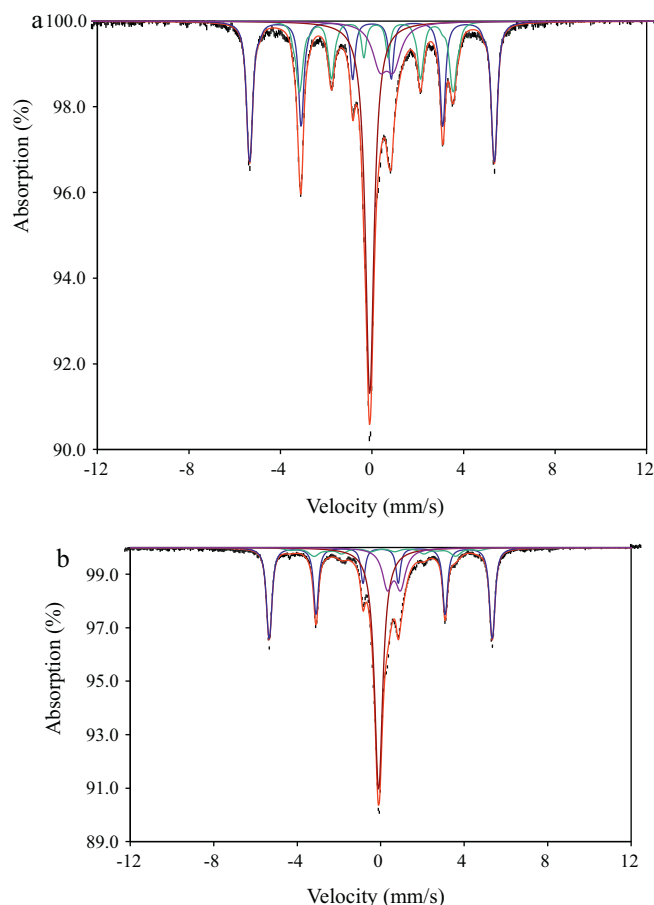


Fig. 4. Mössbauer spectra of a 4%-Fe + 0%-Na catalyst and coal mixture: (a) after pyrolysis at 800 °C, run at 295 K; (b) after 20 min of steam gasification at 800 °C; and (c) ash.

3.2.2. Mössbauer spectroscopy

The fitting parameters of Mössbauer spectra obtained in this study are presented in Table 3. Coal samples without the Fe catalyst were also evaluated with Mössbauer spectroscopy, but there was not enough Fe in them to obtain a spectrum. The spectra related to the catalytic coal mixture 4%-Fe + 0%-Na under different conditions are presented in Fig. 4. Fig. 4a is the spectrum after pyrolysis. A peak comprising 33% of the spectral area was observed with isomer shift (δ) of 0.0 mm/s and quadrupole splitting (Δ) also 0.00 mm/s, indicating metallic Fe, which appears to be the main catalytic species at this point of the process. However, Fe⁵⁺ (δ = −0.10 mm/s and Δ = 0.02 mm/s) is also present as 33% of the total Fe, while 20% of the area is Fe³⁺ in cementite, and the remaining 12% of the total Fe is in an unknown phase with non-specific parameters. The spectrum after 20 min of gasification is presented in Fig. 4b. Here, the proportions of metallic Fe and Fe⁵⁺ increase slightly at the expense of the other doublets.

The Mössbauer spectra of the 2%-Fe + 2%-Na catalyst and coal mixture at different conditions are presented in Fig. 5. Fig. 5a, which presents the catalyst after pyrolysis, shows notable differences compared to the 4%-Fe + 0%-Na at the same condition (Fig. 4a), indicating significantly less presence of Fe as either Fe⁵⁺ or Fe metal. This spectrum is dominated by doublets from cementite and an unassigned doublet, possibly representing Fe species in different oxidation states, i.e., FeO₄ groups and Fe₃C characterized by the smaller peaks. After 20 min of gasification (Fig. 5b), features due to metallic Fe and cementite doublets further decrease in intensity.

Table 3
Mössbauer parameters of reaction products.

Sample		4% Fe pyrolysis	4% Fe 20 min water	3%-Fe + 1%-Na pyrolysis	3%-Fe + 1%-Na 20 min water	2%-Fe + 2%-Na pyrolysis	2%-Fe + 2%-Na 20 min water
Velocity scale (mm/s)		±10	±10	±10	±10	±10	±10
Spectrum temp (K)		295	295	295	295	295	295
Fe ⁵⁺	IS	−0.10	−0.10	−0.11	−0.10	−0.11	−0.10
	QS	0.02	0.00	0.02	0.17	0.00	−0.16
	Width	0.45	0.48	0.46	0.36	0.47	0.32
	Area	33	37	27	16	22	11
Metallic Fe	IS	0.00	0.00	−0.01	0.01	−0.01	−0.01
	QS	0.00	0.01	0.00	−0.01	0.01	0.02
	Width	0.24	0.25 [*]	0.24	0.30 [*]	0.27	0.23 [*]
	Area	33.97	39.70	35.16	21.86	25.25	14.82
Cementite	Field	332	331	331	331	330	331
	IS	0.18	0.15	0.18	0.19	0.19	0.19
	QS	0.01	0.09	0.02	0.02	0.02	0.02
	Width	0.23 [*]	0.55 [*]	0.28	0.26	0.29	0.23 [*]
	Area	20.30	14.65	25.25	30.05	39.59	38.26
	Field	209	209	208	208	208	208
	χ ²	1842.64	4900.73	2975.22	3525.73	1352.57	4076.75
	χ ² _{norm}	3.53	9.31	5.76	6.82	2.64	7.97

IS = isomer shift in mm/s; QS = quadrupole splitting in mm/s; field magnetic field in Oe; Width = FWHM of peaks in mm/s; area is percentage of total spectral area.

^{*} Parameter fixed.

3.2.3. Scanning electron microscopy

Scanning electron microscopy (SEM) images provided further information about the surface. Fig. 6 shows the 4%-Fe + 0%-Na fresh catalyst and coal mixture, in which FeCO₃ could represent the lighter gray particles. The catalytic particles are still present after 20 min of gasification (Fig. 6b), though to a lesser extent. The structures of these composite catalysts are considerably more uniform than those present in the Na catalysts. Conversely, the SEM of the pure Na catalysts presented in Fig. 7a indicates that the structures are noticeably rougher and contain smaller particles. Carbon and graphite decomposition are evident in Fig. 7b, which is an image of the sample after 20 min of gasification.

3.3. Tar characteristics

The effect of Fe catalysts on coal tar breakdown has been widely discussed and conflicting results have been presented. Popa et al. observed that the use of 3 wt% siderite as a catalyst decreases the amount of aromatics in coal tar [29]. Other researchers have indicated that while the Fe catalyzed reaction might increase tar production and enhance syngas production, the composition of the tar does not change significantly and thus no effect was reported [38]. Our current study confirmed that tar composition indeed varies when different catalysts are used. Catalytic tar breakdown could permit lower temperatures for syngas production.

3.3.1. Fourier transform infrared spectroscopy (FTIR)

Fig. 8 shows the FTIR spectrum of the heavy tar fraction for the 2%-Fe + 2%-Na catalyst/coal mixture after pyrolysis at 800 °C. This spectrum is representative of the heavy coal tar produced from the other catalyst and coal mixtures, as no substantial differences were observed among the products from the different catalysts through this technique. Thus, these analyses provide general characteristics of all of the heavy tars. The peaks in Fig. 8 are characteristics of coal tars. For example, two strong peaks at 751 cm^{−1} and 810 cm^{−1} indicate the presence of phenyl monosubstituted rings. Light gas evolution and tar formation during pyrolysis start in the range of 387–687 °C according to Suuberg [39], depending on the coal rank and other process conditions, such as heating rate. Hambly observed that during this initial pyrolysis stage, low-rank, subbituminous coals produce lower amounts of aromatics in their tars compared to their higher rank counterparts [25]. In our research on subbituminous coal, the aromatics to aliphatics ratios varied

with different catalysts, as described in the next section. One of the previous studies performed by our group suggested that the influence of Fe catalysts created a redox mechanism that favored the dehydroxylation of C–OH groups in the tar, thus forming aldehydes and ketones represented by the peak at 1670 cm^{−1} [26,36]. The broad peak at 1300 cm^{−1} indicates the presence of aliphatic methylated chains. Between 1500 cm^{−1} and 3050 cm^{−1}, the majority of the peaks are due to aromatics in the heavy tars. Higher order aromatic and hydroaromatic clusters containing multiple substitutions are formed as their weakest links break to produce aromatic molecular fragments and depolymerization products during pyrolysis [37]. The light tar fractions were not analyzed through FTIR due to the sensitivity of this method to the solvent used to collect the light tar.

3.3.2. Gas chromatography/ mass spectroscopy (GC/MS)

A comparison based on GC/MS analysis of the four light tars obtained from different samples at 800 °C, namely 0%-Fe + 4%-Na (a), 2%-Fe + 2%-Na (b), 4%-Fe + 0%-Na (c), and raw coal (d), is shown in Fig. 9. A key observation among the spectra is that the ratio of heavy to light components increases with Fe loading, as shown by the increase in the size of the peaks at higher retention times for Fig. 9c compared to Fig. 10a,b. Light fractions of the tars were considerably more aliphatic in nature than their heavier counterparts and are produced during earlier stages of devolatilization. The main mass losses that accompany pyrolysis occur in the region of 200 °C to 300 °C, based on TGA analyses of the same catalytic coal mixtures [31,32]. The intensive mass loss produced with Na based catalysts accounts for a rapid tar accumulation.

The GC/MS results for the heavy tars from the same samples are shown in Fig. 10. The results show that larger quantities of heavier components are produced by the Na-based catalysts (Fig. 10a) compared to the Fe catalysts (Fig. 10b and Fig. 11c), which have previously been shown to substantially decrease the production of heavy tars [29]. Fe tar breakdown produced higher ratios of aliphatics to aromatics than the ones obtained with pure Na based catalysts or non-catalytic gasification. The distribution of components in Fig. 10 indicates key differences between the tars; however, important fractions were common among all tars. For example, long aliphatic chains (both alkanes and alkenes, such as retene, octadecane, hexadecane, eicosane, and eneicosane) were observed in all the samples. Their production is caused by the breakdown of aromatic clusters, mainly during the primary pyrolysis dehydration (200 °C–400 °C) [40].

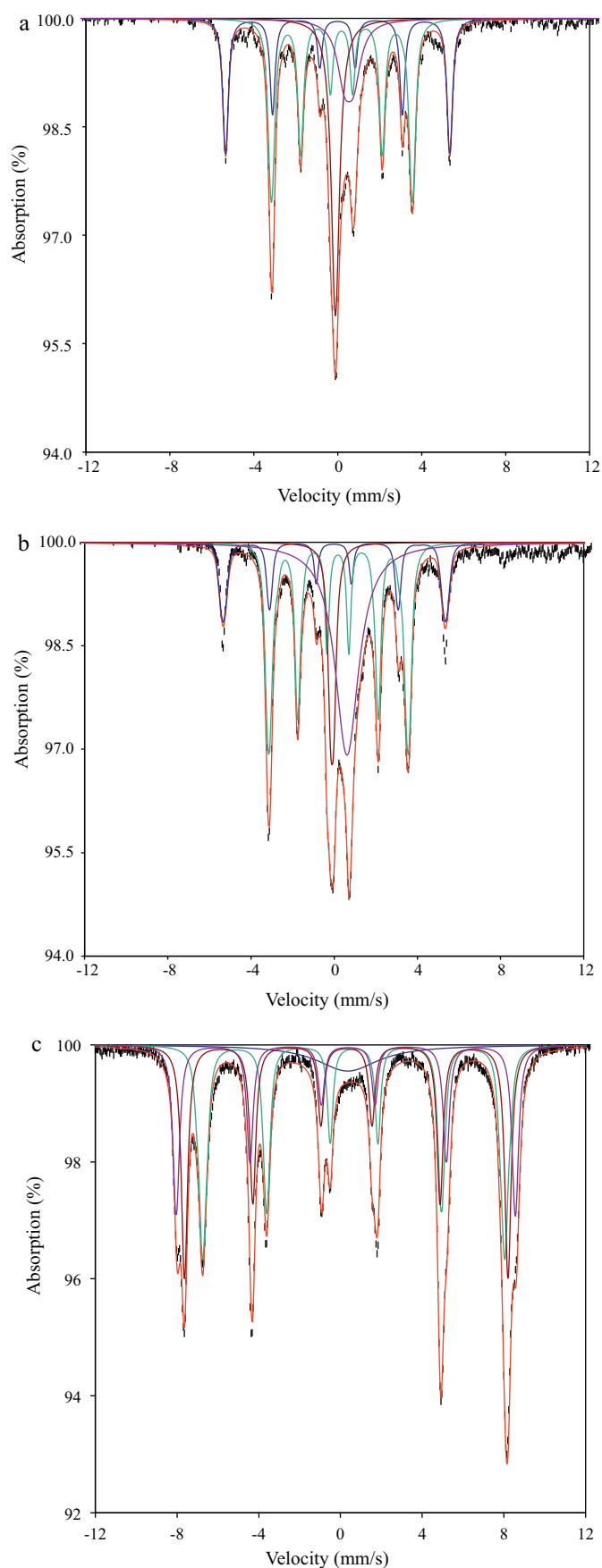


Fig. 5. Mössbauer spectra of a 2%-Fe + 2%-Na catalyst and coal mixture: (a) after pyrolysis at 800 °C, run at 295 K; (b) after 20 min of steam gasification at 800 °C; and (c) ash.

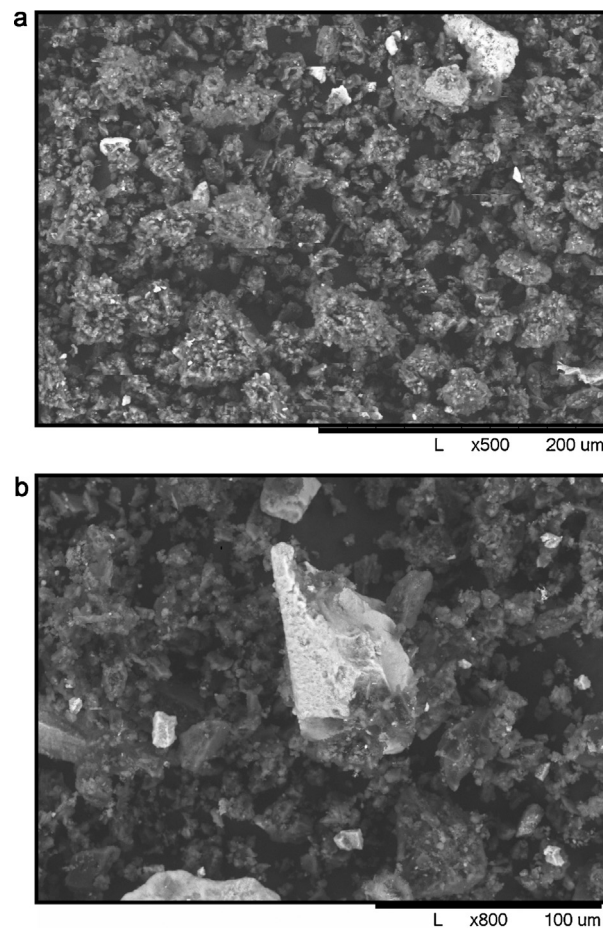


Fig. 6. SEM scan of a 4%-Fe + 0%-Na catalyst and coal mixture: (a) raw and (b) after pyrolysis at 800 °C.

Our prior TGA analyses performed during pyrolysis to maximum temperatures of 400 °C indicate less intense tar formation for the 4%-Fe + 0%-Na and 2%-Fe + 2%-Na catalysts [29,31]. Additionally, the coal tar yield is directly correlated to the presence of donor hydrogen [41], which could be related to the lower tar production with Fe catalysts, since previous results indicated a much higher efficiency of H₂ production with these catalysts [31], resulting in a lower hydrogen content in the tar. The higher yield of H₂ in the syngas with Fe catalysts has been related to the water gas shift reaction on FeO, which produces Fe₃O₄ and H₂. Subsequently, magnetite reacts with CO produced from steam gasification to form FeO and CO₂. Finally, CO₂ is consumed by the Boudouard reaction [29,31]. Lower amounts of hydrogen in the tar, which can be caused by a dehydrogenation mechanism, can lead to the formation of aldehydes, ketones, and alkenes.

Catalytic tar breakdown occurs mainly during secondary pyrolysis at higher temperatures [26], in this case, from 400 °C to 800 °C. As indicated above, in this temperature range, Fe catalysts have the capacity of reducing alcohols, including phenols, thereby producing more molecules containing C=O groups. The data presented in Fig. 10 illustrate this fact. For example, the peak at 16.1 min is associated with benzoic acid, the next three peaks between 16.4 and 16.6 min are associated with ketones, and the peak at 16.7 min is due to acetic acid. These peaks were also observed in all catalysts and raw coal spectra. Our previous FTIR analysis indicated that the tar products of siderite (Fe) catalyzed gasification do not contain as many of C=C aromatics compared to uncatalyzed coal tars [29]. Such decreases appear to occur with Fe–Na composite catalysts. Other examples of carbonyl groups obtained with Fe-based tars

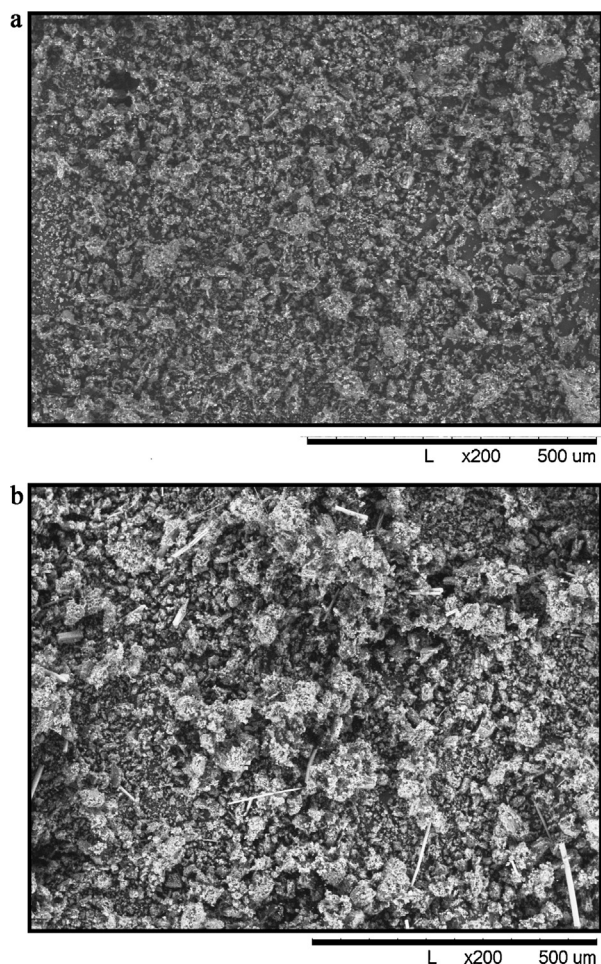


Fig. 7. SEM scan of a 0%-Fe + 4%-Na catalyst and coal mixture: (a) raw and (b) after pyrolysis at 800 °C.

include monosubstituted benzoic acid, 2,1,3-benzoselenadiazole-5-carboxylic acid at 16.9 min (Fig. 10c), and acetic acid, among other species including ketones, which is consistent with this mechanism of conversion of siderite into FeO and Fe₃O₄ in the solid phase. For the 2%-Fe + 2%-Na coal tar, alcohols were not as prevalent compared

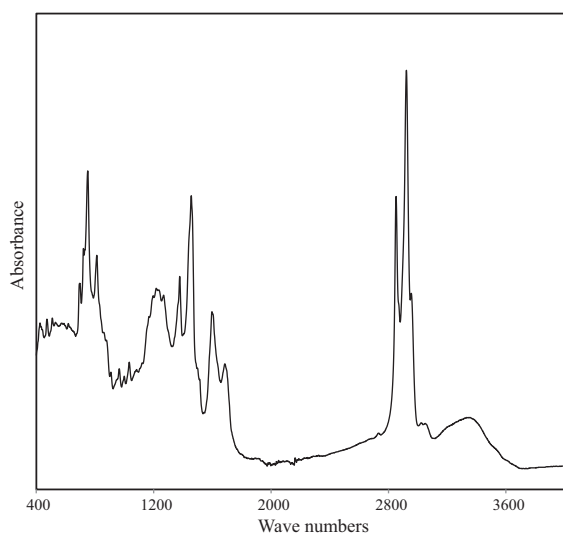


Fig. 8. FTIR spectrum of a 2%-Fe + 2%-Na catalyst heavy tar produced during N₂ pyrolysis conditions at 800 °C.

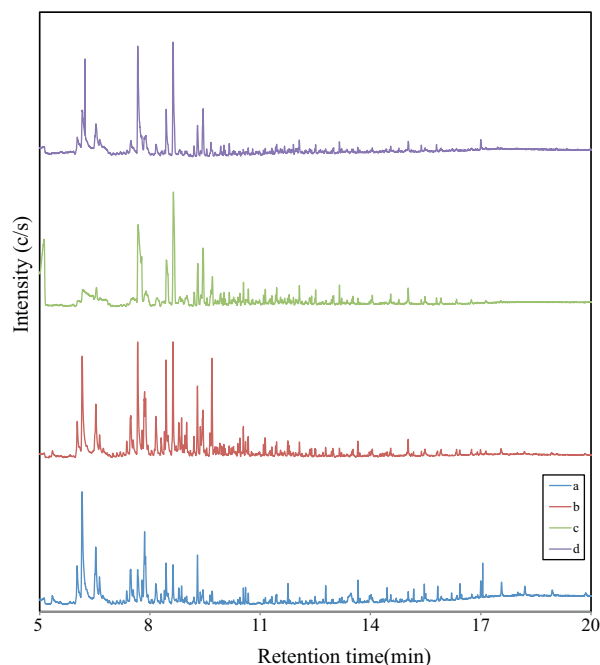


Fig. 9. Gas chromatograms of light tars produced during N₂ pyrolysis at 800 °C: (a) 0%-Fe + 4%-Na, (b) 2%-Fe + 2%-Na, (c) 4%-Fe + 0%-Na, and (d) raw coal.

to Na-based tars. However, few carboxylic acids, aldehydes or ketones were observed in the 2%-Fe + 2%-Na tar, whereas aromatic rings and naphthalenes were still predominant. On the other hand, sodium based tars were dominated by aromatic alcohols (phenol, mono, di and trisubstituted phenols, cresol) and naphthalenes, with some long chain aliphatic compounds such as heneicosane and eicosane. Phenols appeared at 7.75, 8.51, and 8.71 min of retention time (Fig. 10a), which likely correspond to phenol, 2-methyl

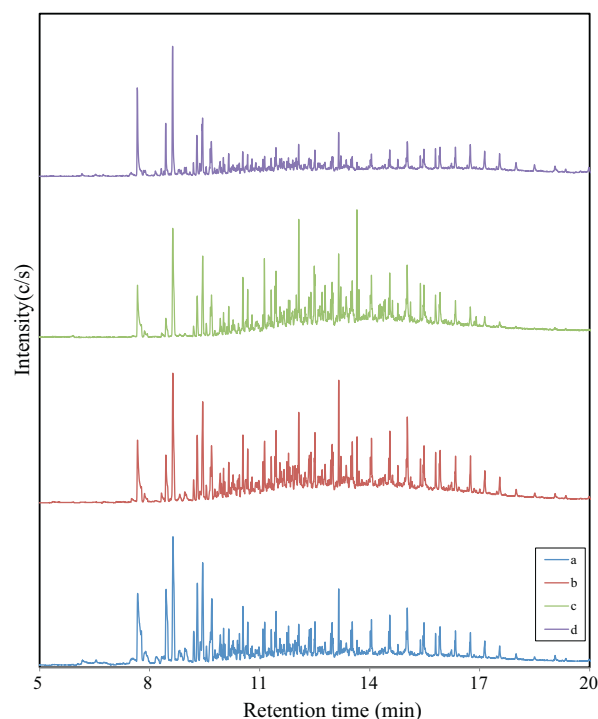


Fig. 10. Gas chromatograms of heavy tars produced during N₂ pyrolysis at 800 °C: (a) 0%-Fe + 4%-Na, (b) 2%-Fe + 2%-Na, (c) 4%-Fe + 0%-Na, and (d) raw coal.

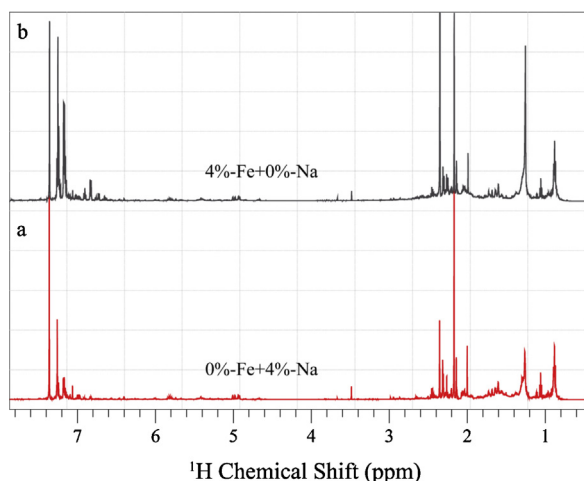


Fig. 11. Overlay of ^1H spectra of light tars produced during N_2 pyrolysis at 800°C : (a) 0%-Fe + 4%-Na and (b) 4%-Fe + 0%-Na.

phenol, and/or 3-methyl phenol. The distinctive peak of *o*-cresol and *p*-cresol appears at 9.51 min.

Given the complexity of the tar mixture, many derivatives can be obtained through further processing, such as hydrocracking or other refining [42]. Thus, many of the specific components in coal tar and the effect of different catalysts on its composition deserve further study. In summary, catalytic dehydrogenation of the tar by iron catalysts results in more carbonyl containing species and alkenes compared to the tars produced by their sodium counterparts. Iron catalysts also increase the production of H_2 in the syngas while reducing the hydrogen content of the tar, and produce lower molecular weight tars compared to tar from the sodium catalysts. Finally, sodium based tars, which are dominated by aromatic rings, are produced during earlier stages of the process, as confirmed by TGA devolatilization results [32]. Faster accumulation and higher yields of tar are related to the initial rate of devolatilization. Composite catalysts provide a method for tailoring the quantity and composition of the coal tar product. When combined with the enhancement of gasification rates that these composite catalysts provide [31], the modification of the tar properties could be very beneficial for the overall process efficiency. Furthermore, based on the tar composition results, the selectivity of the process is altered depending on the catalyst Fe/Na ratios; therefore, the final composition of the tar can be manipulated by varying the catalyst composition to attain the desired products.

3.3.3. Nuclear magnetic resonance (NMR)

NMR spectroscopy is a powerful technique in the characterization of coal and tar samples [43,44]. We used ^1H and ^{13}C solution NMR spectroscopy to compare the composition of light and heavy tars from coal pyrolysis. Samples from four pyrolysis running under different catalytic conditions were compared without catalyst: 0%-Fe + 4%-Na, 2%-Fe + 2%-Na, and 4%-Fe + 0%-Na catalyst. Each experiment yielded a light and heavy tar sample. Our results illustrate that the specific catalyst had a marked qualitative and quantitative effect on the tar hydrocarbon mixtures. The NMR spectra suggest that the composition of the light tars was similar in the four pyrolysis reactions under different catalytic conditions. However, the catalysts strongly influenced the relative ratio and the yield of hydrocarbons. The heavy tars were more diverse and complex than the light tars. The nature of the catalyst had a strong influence on the yield and composition of the hydrocarbon mixture.

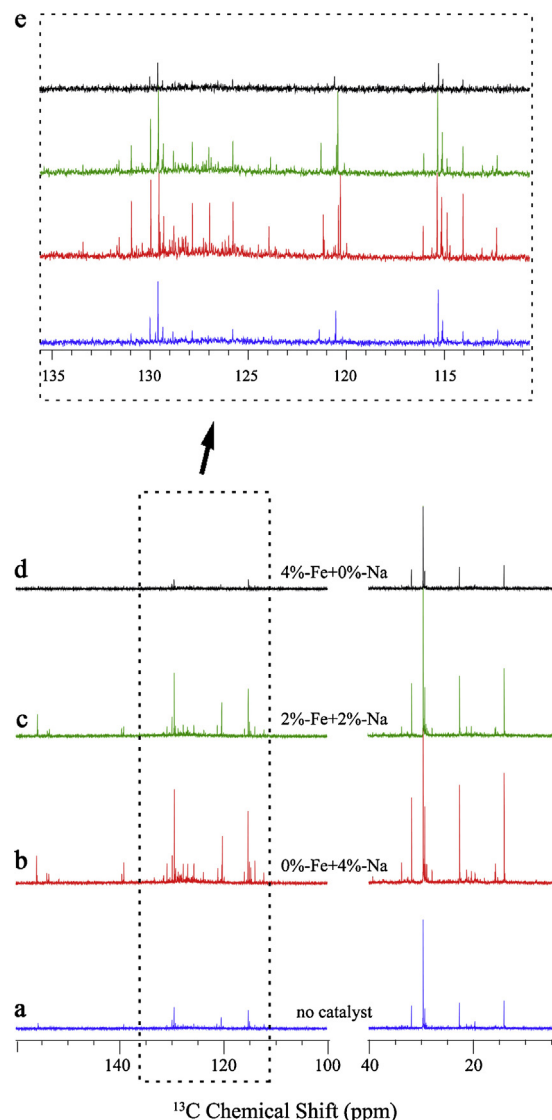


Fig. 12. Overlay of ^{13}C spectra of heavy tars produced during N_2 pyrolysis at 800°C : (a) raw coal, (b) 0%-Fe + 4%-Na, (c) 2%-Fe + 2%-Na, and (d) 4%-Fe + 0%-Na. The aromatic regions of the spectra are enlarged in panel (e).

Given the complexity of the mixtures, both ^1H and ^{13}C NMR spectroscopy were used to confirm the presence of the major classes of organic compounds determined by other methods (vide supra) and to provide insight into the ratio of aromatic and aliphatic components. ^1H and ^{13}C spectra confirmed the presence of phenols. Although detected by FTIR and GC/MS analyses, carboxylic acids and their derivatives were not detected by NMR. The four light tar samples contained a small amount of ketones, (^{13}C δ = 209.9 ppm and 207.2 ppm). No ketones were observed in the heavy tars. The DEPT-135 ^{13}C experiment was used to distinguish carbons with different number of hydrogens attached. CH_3 and CH groups yield positive peaks, while CH_2 groups have negative intensity, and carbons with no attached protons are absent. All samples contained a complex mixture of aromatic compounds. Almost all peaks of the ^{13}C spectra between 110 and 160 ppm were aromatic. One exception was a peak at ~ 114 ppm that had a negative intensity in the DEPT-135 spectra. This peak was identified as a CH_2 group and was tentatively assigned to a terminal aliphatic alkene. None of the peaks between 146–160 ppm were present in the DEPT-135 spectrum; thus, they belong to aromatic carbons that do not have

any hydrogens (e.g. aromatic carbons joined with aliphatic side chains or catacondensed aromatic carbons). In the aliphatic region (2–40 ppm) of the ^{13}C spectra, a number of CH_3 , CH_2 , and CH groups were observed.

For the light tars, increasing amount of iron catalyst correlated with higher ^1H and ^{13}C peak intensities in both the aromatic and aliphatic regions, as illustrated by the ^1H spectra of 0%-Fe + 4%-Na and 4%-Fe + 0%-Na samples in Fig. 11. Integration of ^1H spectra was used to quantify the relative amounts of aromatic (6.05–9.15 ppm), olefinic (4.23–6.05 ppm), and aliphatic (0.2–4.1 ppm) hydrocarbons. Among the light tars, the highest aromatic:aliphatic ratio was observed in the 4%-Fe + 0%-Na tar sample (36.7:100), while the lowest ratio was observed in the 0%-Fe + 4%-Na sample (21.2:100). The residual ^1H chloroform solvent peak overlapped with the aromatic region and slightly contributed to the integral in all the samples. Interestingly, the olefinic region had approximately the same intensity and spectral shape in all the four light tars. In summary, as the iron concentration increased, the yield of both the aliphatic and aromatic compounds increased in the light tars, but the aromatic compounds increased to a larger extent.

On the other hand, for the heavy tars, an increase of sodium (decrease of iron) in the catalyst correlated with higher ^1H and ^{13}C peak intensities and complexity, as shown by the overlay of ^{13}C spectra in Fig. 12. Integration of ^1H peaks suggests that the aromatic:aliphatic ratio was similar for all the four tars, in the range of 20–23:100. However, the tar spectrum of the pure sodium catalyst (0%-Fe + 4%-Na) displayed numerous new peaks in both the ^{13}C aromatic and aliphatic regions that were not present in the spectra of heavy tars produced by either 4%-Fe + 0%-Na catalyst or without catalyst. The aromatic ^{13}C region became markedly complex (Fig. 12e); thus, the data suggest that high sodium content in the catalyst yields a rich mixture of aromatic compounds in the heavy tar. On the other hand, the pure iron catalyst (4%-Fe + 0%-Na) may promote the breakdown of aromatic compounds in the heavy tar, as this spectrum (Fig. 12e top) contained less intensity and lower peak count than the spectrum of the tar that was produced without a catalyst (Fig. 12e bottom). In summary, the NMR data confirmed that tar compositions can be changed by varying the pyrolytic mechanism through catalysts.

4. Conclusions

Composite catalysts can overcome and enhance the catalytic effects of separate Na and Fe catalysts for coal gasification. Most of the catalytic species appear to be produced at the same stages of pyrolysis and gasification with composite catalysts and pure catalysts. However, some important differences are observed during the last stages of the process, such as active Fe species that appear to enhance the effect of Na based catalysis. Furthermore, Na–Fe oxides appear to form during final gasification phases, which could account for the synergy of the Fe/Na catalysts. Iron oxides were observed on the char surface at later gasification stages, which suggest again that iron catalysts are more active during this phase than sodium catalysts. The catalytic activity of siderite for pure and composite catalysts was confirmed through the presence of metallic iron initially, and cementite at advanced stages of gasification. Monosubstituted phenyl rings among many other aromatics, carbonyl functional groups, and aliphatic chains were primary components of all heavy tars. Fe catalysts showed higher capability for tar decomposition than the other catalysts, producing carboxylic acids, aldehydes and ketones that were not observed in Na-based tars. Understanding the aforementioned characteristics and mechanism of the catalytic PRB coal gasification will be beneficial to optimization of reaction conditions and thus design of coal to liquids process.

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