Petroleum Coke Combustion in Fixed Fluidized Bed Mode in the Presence of Metal Catalysts

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ABSTRACT: Petroleum coke is one of the waste products generated in the oil refining industry that can be used as fuel in energetics. However, the low volatile matter content and graphite-like structure of petroleum coke are the reasons for its high ignition temperature and combustion complexity. In this research, petroleum coke combustion and oxidation kinetics in the presence of metal catalysts were investigated. To evaluate the effect of the catalyst on the ignition temperature and the apparent activation energy, a new approach of a “fixed fluidized bed” was proposed. In this mode, petroleum coke particles spaced from each other by inert quartz powder kind of “freeze” in the porous layer. This regime allows us to determine the ignition temperature of petroleum coke particles in the static mode by differential thermography and calculate the activation energy by gas analysis. Organic and inorganic salts of copper, iron, and cerium are used as catalysts for petroleum coke combustion. A series of experiments were carried out in the porous media thermo-effect cell (PMTEC) and on a thermogravimetric (TG) analyzer. The kinetics of the combustion processes was calculated by Kissinger–Akahira–Sunose and Ozawa–Flynn–Wall methods. The results obtained in the “fixed bed” mode showed that the ignition temperature and the average apparent activation energy significantly decreased in the presence of CuCl₂ and FeCl₃. The results obtained by the new approach were compared with the results of the thermogravimetric analysis.

1. INTRODUCTION

The production of petroleum coke (pet coke), as a byproduct of deep oil refining, is increasing along with the increasing production of petroleum products. However, due to an increase in heavy oil refining, the output of petroleum coke per unit of refined oil is also increasing.

Petroleum coke is mainly used in metallurgy as a carbon source, in the cement industry, for the production of electrodes, and as a fuel in the energy sector. However, the presence of heavy metals and the large sulfur content in its composition limit the use of petroleum coke as a carbon source.

Due to its low cost and relatively high calorific value, petroleum coke is more often used in the energy sector as fuel. For the complete combustion of petroleum coke, the most rational approach is to burn them in boilers with fluidized bed furnaces. Due to the low content of volatile substances and the graphite structure of carbon in petroleum coke, there are problems with its ignition and stable combustion. Partly, these problems can be solved by co-burning petroleum coke with coal or using various catalysts based on lanthanides, and transition and alkali metals.

Since the structure of petroleum coke is mostly graphite-like, we assume that catalysts effectively used in the oxidation of graphite can be tested in the combustion of petroleum coke. High catalytic activity in the processes of graphite oxidation of copper oxides along with oxides of other transition metals...
helps to decrease the ignition temperature significantly.\textsuperscript{10} Also, the results of studies of combustion processes of some carbon-containing substances, such as soot, allow us to conclude about the activity of catalysts based on transition-metal oxides and lanthanides, such as iron, copper, and cerium oxides.\textsuperscript{8,11–14} In addition to oxides, transition-metal chlorides are also highly active in the oxidation of carbon-containing substances.\textsuperscript{5,16}

Thermogravimetric (TG) analysis is usually used to study the combustion process and calculate the kinetic parameters of solid fuels, such as coal and petroleum coke.\textsuperscript{17–22} However, TG experiments have drawbacks such as diffusion of gases inside and outside the sample layer and the relatively small sample mass.\textsuperscript{23,24} Thus, it cannot be used to comprehensively describe the burning of petroleum coke in the fluidized bed mode.

The combustion of petroleum coke in the fluidized bed mode can be studied on full-scale installations simulating the operation of boilers and in small-scale fluidized bed reactors.\textsuperscript{25–31} The advantages of small-scale fluidized bed reactors are the absence of high values and gradients of temperature, more homogeneous conditions, the lower impact of external conditions, simple experiments, and the requirement of a small amount of sample and catalyst for study. Thus, the testing of catalysts will last a shorter time, and it is possible to conduct a larger number of experiments under various conditions.

However, even in the small-scale fluidized bed combustors, the study of the combustion stages is complicated due to a high gas flow rate and a complex velocity profile. Complex motion makes it impossible to measure the ignition temperature of the petcoke particles and compare the experimental results. To measure temperatures of the individual particles during the combustion process, it is necessary to “freeze” the motion of the particle. It can be solved by fixing particles of petcoke in space and creating a “fixed fluidized bed” layer. It allows us to easily determine the ignition temperature and evaluate the effect of the catalyst at a certain stationary point.

In this work, a new approach of a fixed fluidized bed was proposed for studying petroleum coke combustion and the evaluation of the effect of catalysts. To create a fixed bed, petroleum coke was mixed with an inert medium—fine-grained quartz sand. The particles of petroleum coke remain static and are spaced from each other, simulating a fixed fluidized bed. In this mode, we can easily analyze the combustion process and evaluate the behavior of the catalyst at a certain point. For testing the functional ability of the new approach, experiments to evaluate the effect of organic and inorganic salts of copper, iron, and cerium on the petroleum coke combustion were carried out. The data obtained by the new approach were compared with the results of the thermogravimetric analysis.

2. MATERIALS

The petroleum coke used in the experiments was obtained at the delayed coker unit in the TANECO refinery, Russia.

The characteristics of petroleum coke obtained by bomb calorimetry and ultimate and proximate analyses are presented in Table 1.

| ultimate analysis | content (wt %) |
|-------------------|--------------|
| carbon            | 89.7         |
| hydrogen          | 3.9          |
| sulfur            | 4.0          |
| nitrogen          | 0.87         |
| oxygen            | 1.1          |

 proximate analysis | content (wt %) |
|-------------------|--------------|
| moisture          | 1.04         |
| volatiles         | 9.3          |
| ash               | 0.44         |
| fixed carbon      | 89.22        |
| high heating value| 31.8 MJ/kg   |

Table 1. Characteristics of Petroleum Coke

![XRD spectra of petroleum coke](https://dx.doi.org/10.1021/acsomega.0c02250)

Figure 1. XRD spectra of petroleum coke.

Organic and inorganic salts of copper, iron, and cerium were used as potential catalysts for the oxidation of petroleum coke (Table 2). The concentration of catalysts was 1% by weight of petroleum coke in the sample. Low boiling organic solvents such as acetone and dichloromethane were used to improve the mixing of catalysts and petroleum coke samples, which subsequently evaporated from the sample, on heating to 50–70 °C.

Table 2. Catalysts Used in the Experiments

| catalyst formula | catalyst name | source        | purity (%) |
|------------------|---------------|---------------|------------|
| CuCl2            | copper(II) chloride | Sigma-Aldrich | 99         |
| Cu(C10H8O2)2     | copper(II) stearate | Sigma-Aldrich | 99         |
| FeCl3            | iron(III) chloride | Sigma-Aldrich | 97         |
| Fe(C10H8O2)3     | iron(III) stearate | Macklin      | 98         |
| CeCl3            | cerium(III) chloride | Sigma-Aldrich | 99         |
| Ce(C10H8O2)3     | cerium(III) stearate | synthesized | 98         |

3. EXPERIMENTAL PROCEDURE

3.1. Porous Media Thermo-Effect Cell. A porous media thermo-effect cell (PMTEC) was used to implement a fixed fluidized bed mode for petroleum coke combustion. A prototype of this setup was the quartz combustion tube used to study the thermal effect and the influence of the catalyst on the combustion of hydrocarbons in porous media.\textsuperscript{35,34}

The experimental setup consists of a quartz tube reactor with an external diameter of 23 mm, a wall thickness of 5 mm (Figure 2), and an external electric heater with a programmable PID controller. The heater was controlled by a type K...
thermocouple temperature placed inside. At the ends of the quartz tube are sealed metal fittings with holes for thermocouples, as well as for air supply and the exit of combustion products. Type K thermocouples in a ceramic shell with an external diameter of 4 mm were used.

Air was supplied from the air tank. Air pressure was regulated by a two-stage pressure valve. Air flow was measured and regulated by an air rotameter with a needle valve. The concentrations of CO, CO₂, and O₂ in the combustion products were determined by a gas analyzer (MRU, Germany) with built-in Peltier elements cooling the gas to a temperature of 5 °C to remove the condensate.

For experiments, petroleum coke and quartz sand were separately milled, screened to a particle size of 63−100 μm, and mechanically thoroughly mixed in a ratio of 1:5. The sample mass was 0.5 g (0.1 g of petroleum coke and 0.4 g of quartz sand).

To estimate the ignition temperature and the thermal effect of the combustion process in an inert medium, the samples were placed in a quartz tube with external electric heating. The tube was filled by layers: coarse-grained quartz sand, fine-grained quartz sand, sample—fine-grained quartz sand with petroleum coke, fine-grained quartz sand, and coarse-grained quartz sand. Each layer is filled up to a certain level, tamped, and distributed evenly by vibration. Fine-grained quartz sand was used to create an inert layer and hold a sample layer. Coarse-grained quartz sand was used to hold middle layers and allow air to easily penetrate through the tube.

The permeability of the sample allowed air to penetrate easily through the filled tube and react with petroleum coke. Due to the porous medium, the air flow is laminar, with smoothed velocity profiles. Assuming that petroleum coke is perfectly mixed with quartz sand in a ratio of 1:5, the distance between two particles of petroleum coke is 2−3 particles of sand with an average size of 123−200 μm.

The first thermocouple was placed in the middle of the pure fine-grained quartz sand layer before the sample. It showed the temperature inside the tube (internal temperature, T₁) without the combustion thermal effect. The second thermocouple was located in the middle of the sample layer (sample temperature, T₂). The temperature difference between T₁ and T₂ showed the thermal effect of the combustion process (temperature difference, T₃). After filling the tube and fixing of thermocouples, the fittings at the ends were tightly closed, and the tube was installed in an electric heater. The heating program was set to preheat up to 40 °C, followed by a subsequent linear increase in temperature up to 700 °C.

An example of the temperature profiles of a PMTEC pure petcoke combustion experiment at the heating rate of 10 °C/min is shown in Figure 3. The atmospheric-pressure air flow rate was 0.3 L/min.

3.2. Thermogravimetric Analysis. To compare the results obtained in the PMTEC, a thermogravimetric analysis of the petroleum coke oxidation was carried out. A TG 209F1 Libra thermogravimeter (NETZSCH GmbH) combined with an α Fourier-transform infrared spectrometer (FTIR) (Bruker GmbH) calibrated by six melting points of high-purity metals (In, Sn, Bi, Zn, Al, Au) by c-DTA using ASTM E1582-17 and 200 μL of a corundum (Al₂O₃) crucible was used for this task. Experiments were carried out according to ASTM E2105-00 (2016). For measurements, the same mixture of petroleum coke with fine-grained quartz sand (ratio 1:5) as in PMTEC was used. The sample mass was 100 mg. The chosen heating rates were 6, 8, 10, and 12 °C/min. The air flow rate was 30 mL/min, and the protective gas flow rate for the furnace (nitrogen) was 45 mL/min.

3.3. Kinetic Calculations. The apparent activation energy (Eₐ) of petroleum coke combustion was calculated using the Kissinger–Akahira–Sunose (KAS) 35 and Ozawa–Flynn–Wall (OFW) 36,37 kinetic isoversional methods. The KAS method is based on eq 1.
\[
\ln\left(\frac{\beta}{T_{ai}}\right) = \ln \left(\frac{A_e R}{E_{g}(\alpha)} - \frac{E_a}{R T_{ai}}\right)
\]

where \( \beta \) is the heating rate (°C/min), \( T \) is the temperature for a definite conversion degree (\( \alpha \)), \( A_e \) is the pre-exponential factor or Arrhenius constant (s^{-1}), \( R \) is the universal gas constant (8.314 J/mol K), \( E_a \) is the apparent activation energy for a definite conversion degree \( \alpha \), and \( g(\alpha) = \int_0^\infty \frac{dt}{\alpha(\alpha)} \) is the integral function depending on the reaction model.

The KAS method allows us to estimate the value of the apparent activation energy from a plot of \( \ln(\beta/T_{ai}) \) against \( 1000/T \) for a series of data with different heating rates \( \beta \). The slope of such isoconversional straight lines is equal to \(-E_a/R\).

The OFW method is based on a similar equation as follows

\[
\ln(\beta) \equiv -1.0522 \left(\frac{1}{T_{ai}}\right) - 5.33 - \ln\left[\frac{AE_a}{R g(\alpha)}\right]
\]

The value of the apparent activation energy can be calculated from the slope of a plot of \( \ln(\beta) \) against \( 1000/T \) for each given conversion degree.

The conversion degree in PMTEC experiments was estimated using the following expression

\[
X(t) = \frac{\int_0^t ((CO + CO_2) - CO_2^0)}{\int_0^\infty ((CO + CO_2) - CO_2^0)}
\]

where \( CO_2^0 \) is the initial concentration of carbon dioxide in the air (vol %); \( CO_2 \) and \( CO \) are the concentrations of carbon monoxide and dioxide (vol %) at a definite moment (\( t \)).

For TG experiments, the conversion degree was defined as the partial mass loss using the following eq 4

\[
X(t) = \frac{m_0 - m_t}{m_0 - m_{\infty}}
\]

where \( m_0, m_t, \) and \( m_{\infty} \) are the masses of petroleum coke that correspond to the initial period, definite moment, and the end of the experiment, respectively.

4. RESULTS AND DISCUSSION

Petroleum coke has a high heating value and low price, which are good properties for power plant fuels. However, the low content of volatile substances and the graphite-like carbon structure impede the combustion of coke; only the use of catalysts can reduce the ignition temperature and stabilize the combustion process. According to the composition and structure of petroleum coke, transition metals and lanthanides, effectively used in the oxidation of graphite and soot such as copper, iron, and cerium, can affect the ignition temperature of pet coke. Stearic acid was used as an organic anion to achieve catalyst solubility and increase heat release in the low-temperature zone. Metal chlorides were tested as prospective carbon oxidation catalysts.15,16,38

The proposed fixed fluidized bed approach implemented in the PMTEC setup allows one to quickly and fairly evaluate the effect of catalysts on the ignition temperature of the combustion process under conditions close to those of a fluidized bed combustion mode.

4.1. PMTEC Results. To test the fixed fluidized bed mode, experiments were carried out with pure petroleum coke as a blank sample, and several catalysts (Table 2). To speed up result acquisition, a preliminary analysis of the chosen catalysts in PMTEC was carried out at a heating rate of 15 °C/min. The atmospheric-pressure air flow rate was 3 L/min. Figure 4 shows a graph of the temperature difference \( (T_d) \), the result of the combustion thermal effect, versus the internal temperature \( (T_i) \).

A small decrease in the temperature in the region of \( T_i = 100 \) °C is associated with the evaporation of water from the sample. A decrease in the ignition temperature of petroleum coke in the presence of CuCl2 and FeCl3 was observed. Other catalysts showed no effect on the ignition temperature. The maximum combustion thermal effect \( (T_d) \) was shown by copper chloride and cerium stearate. More detailed temperature data is shown in Table 3.

![Figure 4. Temperature profiles at a heating rate of 15 °C/min.](https://dx.doi.org/10.1021/acsomega.0c02250)

Table 3. PMTEC Temperature Data

| sample          | onset temperature \( T_i \) (°C) | maximum thermal effect \( T_d \) (°C) |
|-----------------|---------------------------------|-------------------------------------|
| pet coke        | 373                             | 245                                 |
| CuCl2           | 287                             | 415                                 |
| FeCl3           | 306                             | 311                                 |
| Fe(C12H22O2)    | 371                             | 251                                 |
| Cu(C12H23O2)    | 376                             | 326                                 |
| Ce(C12H23O2)    | 381                             | 398                                 |
| CeCl3           | 384                             | 314                                 |

For a more detailed investigation of the ignition and combustion of petroleum coke with and without the addition of copper and iron chlorides, experiments were carried out at a lower heating rate of 10 °C/min with the analysis of gas-phase combustion products. The contents of oxygen \((O_2)\), carbon dioxide \((CO_2)\), and carbon monoxide \((CO)\) in evolved gases were analyzed.

The results of PMTEC experiments at a 10 °C/min heating rate showed (Figure 5) that the ignition temperature (onset temperature) decreases significantly in the presence of CuCl2 (decreased by 70 °C) and FeCl3 (decreased by 79 °C) in comparison to pure petroleum coke. A small peak at 300 °C in the presence of iron chloride was noted. According to Figure 7, at this temperature, CO and CO2 start to evolve, and the O2 concentration decreases, which corresponds to the first stage of the combustion process. This effect appears more clearly at heating rates of less than 10 °C.

The most plausible explanation of reactivity of CuCl2 and FeCl3 is their in situ transformation to their corresponding oxychloride forms15,36,39 with high catalytic activity, as
Cu₂OCl₂ and FeOCl, respectively, at about 300 °C. The mechanism of both metal chloride oxidation processes involves two stages: conversion into oxychloride species and then decomposition into metal oxides.¹⁵,³⁹

The graphs in Figures 6−8 show a profile of the combustion thermal effect T_d and the concentrations of CO, CO₂, and O₂ in the gas-phase combustion products. The CO/CO₂ ratio in the combustion products is reduced by 32% in the presence of FeCl₃ and by 46% in the presence of CuCl₂ compared to pure petroleum coke combustion. This proves the effect of the catalyst on the completeness of combustion.

4.2. TG Results. TG−DTG curves of pure petroleum coke combustion and in the presence of a catalyst at the heating rate of 10 °C/min are shown in Figure 9. The results of the thermogravimetric analysis confirmed the catalytic effect of copper and iron chlorides (Table 4). In the temperature range from 30 to 250 °C, a small amount of adsorbed water was evaporated from the sample. At the temperature range of 200−350 °C, the oxidation process of metals included in petroleum coke is observed, which is confirmed by a mass increase. The ignition (T_i) and burnout (T_b) combustion temperatures were determined according to data of CO and CO₂ gas release from FTIR analysis. DTG peak temperature (T_p) was determined by the lowest DTG value.

4.3. Kinetics. The model-free method allows for calculation of the apparent activation energy without the assumption of a

Table 4. General Thermochemical Parameters of the Oxidation Process

| sample   | T_i (°C) | T_p (°C) | T_b (°C) | Δm (%) (350−530 °C) | residual mass (%) |
|----------|---------|---------|---------|---------------------|------------------|
| Petcoke  | 301     | 581     | 870     | 2.79                | 79.79            |
| CuCl₂    | 244     | 582     | 845     | 4.22                | 80.29            |
| FeCl₃    | 294     | 583     | 847     | 5.82                | 80.48            |

10 °C/min
specific reaction model. A comparison of average activation energy helps to evaluate the effect of the catalyst on the petroleum coke combustion process. The isoconversional curves obtained in the PMTEC experiments are shown in Figures 10–12. The conversion degree was related to CO and CO₂ concentrations of eq 3 in the gas products, i.e., carbon oxidation.

To plot the apparent activation energy dependencies (Figures 13–15), experiments were conducted on PMTEC and TG at three heating rates of 8, 10, and 12 °C/min. The conversion degree ranges from 0.15 to 0.9 and data outside this range should be discarded as they are unreasonable. The obtained activation energies of pure petroleum coke are in good agreement with the data of other authors.29,40 Figure 15 clearly shows a decrease in the activation energy of the FeCl₃ sample in PMTEC experiments in the conversion degree range of 0.1–0.35. This correlates with the first temperature peak of T_d in the presence of FeCl₃ (Figure S) and confirms its catalytic effect at these temperatures. TG
experiments did not show the same results (Figure 9). Such differences can be described as gas flux features of TG and also progress of the reaction at these temperatures without mass change but with oxygen consumption.

Kinetics calculation results for both TG and PMTEC experiments showed a decrease in the average activation energy in the presence of catalysts (Table 5). The presence of CuCl2 decreased the average activation energy by 41% (OFW) and 57.5% (KAS) in the PMTEC experiments, and by 13.7% (OFW) and 21.2% (KAS) in the TG experiments. In the presence of FeCl3, the average activation energy decreased by 35.4% (OFW) and 49.6% (KAS) in the PMTEC experiments, and by 10.4% (OFW) and 2.5% (KAS) in the TG experiments.

From the OFW kinetic pattern obtained in the PMTEC experiments (Figure 16), it can be seen that FeCl3 affects the first stage of the oxidation reaction ($\alpha = 0.1$–0.35) to a greater extent than CuCl2. However, in the 0.4–0.9 conversion degree range, CuCl2 decreases the activation energy to a slightly greater extent. It will be interesting to see the synergy effect of both these catalysts in further investigations.

5. CONCLUSIONS

In this paper, the characteristics and kinetics of petroleum coke combustion in the presence of catalysts were investigated. The main conclusions are as follows:

(1) The new approach to study petroleum coke combustion by the fixed fluidized bed was presented. This approach allows us to determine the ignition temperature of petroleum coke particles in stationary mode and evaluate the efficiency of catalysts through a differential thermogram and apparent activation energy by analyzing the composition of the gas-phase combustion products.

(2) PMTEC experiments showed that copper(II) chloride and iron(III) chloride brought about a higher decrease in the ignition temperature of petroleum coke. Gas analysis of the combustion products indicated that the CO/CO2 concentration ratio decreased in the presence of these catalysts.

(3) TG experiments confirmed that the ignition temperature decreased in the presence of CuCl2 and FeCl3. Catalysts have the greatest effect on the first stage of combustion in the temperature range of 350–530 °C.

(4) Apparent activation energies for blank petroleum coke and in the presence of FeCl3 and CuCl2 as catalysts were obtained by the OFW and KAS methods in the PMTEC and TG experiments for three heating rates: 8, 10, and 12 °C/min. It is shown that in the presence of CuCl2 and FeCl3, the average apparent activation energy of the petroleum coke oxidation decreases.

### Table 5. Kinetic Parameters for Petcoke Combustion

| Sample          | Average $E_a$ (OFW) (kJ/mol) | Average $E_a$ (KAS) (kJ/mol) |
|-----------------|-------------------------------|-----------------------------|
| Pure petcoke    | 105.1                         | 136.5                       |
| 1% CuCl2        | 61.9                          | 57.9                        |
| 1% FeCl3        | 67.9                          | 68.7                        |

CuCl2 decreased the activation energy by 41% (OFW) and 57.5% (KAS) in the PMTEC experiments, and by 13.7% (OFW) and 21.2% (KAS) in the TG experiments. In the presence of FeCl3, the average activation energy decreased by 35.4% (OFW) and 49.6% (KAS) in the PMTEC experiments, and by 10.4% (OFW) and 2.5% (KAS) in the TG experiments.

Figure 16. Comparison of the apparent activation energies of pure petcoke combustion and in the presence of FeCl3 and CuCl2 obtained from PMTEC experiments by the OFW method.

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c02250

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Mancuso, L.; Arienti, S. Petroleum Coke (Petcoke) and Refinery Residues. *Integr. Gasif. Comb. Cycle (IGCC) Technol.* 2017, 121–14.

(2) Tao, W. Managing China’s Pet coke Problem; Carnegie Endowment for International Peace, 2015; pp 1–34.

(3) Shan, Y.; Guan, D.; Meng, J.; Liu, Z.; Schroeder, H.; Liu, J.; Mi, Z. Rapid Growth of Petroleum Coke Consumption and Its Related Emissions in China. *Appl. Energy* 2018, 226, 494–502.

(4) Chen, J.; Lu, X. Progress of Petroleum Coke Combustion in Circulating Fluidized Bed Boilers-A Review and Future Perspectives. *Resour. Conserv. Recycl.* 2007, 49, 203–216.

(5) Bryers, R. W. Utilization of Petroleum Coke and Petroleum Coke/Coal Blends as a Means of Steam Raising. *Fuel Process. Technol.* 1995, 44, 121–141.

(6) Jun, M. L.; James, J. B.; Jeffery, G. R.; Robert, L. Comparison of Fuel Properties of Petroleum Cokes and Coals Used in Power Generation. *Fuel Energy Abstr.* 1999, 40, 418.
(7) Walsh, D. E.; Green, G. J. A Laboratory Study of Petroleum Coke Combustion: Kinetics and Catalytic Effects. *Ind. Eng. Chem. Res.* 1988, 27, 1115–1120.

(8) Sudarsanam, P.; Hillary, B.; Deepa, D. K.; Amin, M. H.; Mallesh, B.; Reddy, B. M.; Bhargava, S. K. Highly Efficient Cerium Dioxide Nanocube-Based Catalysts for Low Temperature Diesel Soot Oxidation: The Cooperative Effect of Cerium- and Cobalt-Oxides. *Catal. Sci. Technol.* 2015, 5, 3496–3500.

(9) Li, Y.; Yang, H.; Hu, J.; Wang, X.; Chen, H. Effect of Catalysts on the Reactivity and Structure Evolution of Char in Petroleum Coke Steam Gasification. *Fuel* 2014, 117, 1174–1180.

(10) Neef, J. P. A.; Makkee, M.; Moulijn, J. A. Metal Oxides as Catalysts for the Oxidation of Soot. *Chem. Eng. J. Biochem. Eng. J.* 1996, 64, 295–302.

(11) Stanmore, B. R.; Brilliac, J. F.; Gilot, P. The Oxidation of Soot: A Review of Experiments, Mechanisms and Models. *Carbon* 2001, 39, 2247–2268.

(12) Mul, G.; Neef, J. P. A.; Kapteijn, F.; Makkee, M.; Moulijn, J. A. Soot Oxidation Catalyzed by a Cu/K/Mo/Cl Catalyst: Evaluation of the Chemistry and Performance of the Catalyst. *Appl. Catal., B* 1995, 6, 339–352.

(13) Bonnefoy, F.; Gilot, P.; Stanmore, B. R.; Prado, G. A Comparative Study of Carbon Black and Diesel Soot Reactivity in the Temperature Range 500-600°C Effect of Additives. *Carbon* 1994, 32, 1333–1340.

(14) Salvat, O.; Marez, P.; Belot, G. Passenger Car Serial Application of a Particulate Filter System on a Common Rail Direct Injection Diesel Engine. *SAE Tech. Pap.* 2000, 109, 227–239.

(15) Fujimoto, T.; Takaoka, M. Direct Chlorination of Carbon by Copper Chloride in a Thermal Process. *Environ. Sci. Technol.* 2009, 43, 2241–2246.

(16) Zou, X.; Yao, J.; Yang, X.; Song, W.; Lin, W. Catalytic Effects of Metal Chlorides on the Pyrolysis of Lignite. *Energy Fuels* 2007, 21, 619–624.

(17) Jayaraman, K.; Kok, M. V.; Gokalp, I. Pyrolysis, Combustion and Gasification Studies of Different Sized Coal Particles Using TGA-MS. *Appl. Therm. Eng.* 2017, 125, 1446–1455.

(18) Zou, J. H.; Zhou, Z. J.; Wang, F. C.; Zhang, W.; Dai, Z. H.; Liu, H. F.; Yu, Z. H. Modeling Reaction Kinetics of Petroleum Coke Gasification with CO2. *Chem. Eng. Process.* 2007, 46, 630–636.

(19) Jayaraman, K.; Kok, M. V.; Gokalp, I. Thermogravimetric and Mass Spectrometric (TG-MS) Analysis and Kinetics of Coal-Biomass Blends. *Renewable Energy* 2017, 101, 293–300.

(20) Yao, H.; He, B.; Ding, G.; Teng, W.; Kuang, Y. Thermogravimetric Analyses of Oxy-Fuel Co-Combustion of Semi-Coke and Bituminous Coal. *Appl. Therm. Eng.* 2019, 156, 708–721.

(21) Hu, L.; Zhang, Y.; Chen, D.; Fang, J.; Zhang, M.; Wu, Y.; Zhang, H.; Li, Z.; Lyu, J. Experimental Study on the Combustion and NOx Emission Characteristics of a Bituminous Coal Blended with Semi-Coke. *Appl. Therm. Eng.* 2019, 160, No. 113993.

(22) Govindan, B.; Chandra Babu Jamma, S.; Radhakrishnan, T. K.; Tiwari, A. K.; Sudhakar, T. M.; Shanmugavelu, P.; Kalburgi, A. K.; Sanyal, A.; Sarkar, S. Investigation on Kinetic Parameters of Combustion and Oxy-Combustion of Calcined Pet Coke Employing Thermogravimetric Analysis Coupled to Artificial Neural Network Modeling. *Energy Fuels* 2018, 32, 3995–4007.

(23) Salvador, S.; Commandré, J. M.; Stanmore, B. R. Combustion Rates for the Oxidation of Highly Sulphurised Petroleum Cokes: The Influence of Thermogravimetric Conditions and Some Coke Properties. *Fuel* 2003, 82, 715–720.

(24) Song, Q.; He, B.; Yao, Q.; Meng, Z.; Chen, C. Influence of Diffusion on Thermogravimetric Analysis of Carbon Black Oxidation. *Energy Fuels* 2006, 20, 1895–1900.

(25) Shen, L.; Wu, J.; Xiao, J.; Song, Q.; Xiao, R. Chemical-Looping Combustion of Biomass in a 10 kWt Reactor with Iron Oxide as an Oxygen Carrier. *Energy Fuels* 2009, 23, 2498–2505.

(26) Lind, F.; Seemann, M.; Thueman, H. Continuous Catalytic Tar Reforming of Biomass Derived Raw Gas with Simultaneous Catalyst Regeneration. *Ind. Eng. Chem. Res.* 2011, 50, 11553–11562.

(27) Adánez, J.; Gayán, P.; Celaya, J.; De Diego, L. F.; García-Labiano, F.; Abad, A. Chemical Looping Combustion in a 10 kWt Prototype Using a CuO/Al2O3 Oxygen Carrier: Effect of Operating Conditions on Methane Combustion. *Ind. Eng. Chem. Res.* 2006, 45, 6075–6080.

(28) Yu, J.; Yue, J.; Liu, Z.; Dong, L.; Xu, G.; Zhu, J.; Duan, Z.; Sun, L. Kinetics and Mechanism of Solid Reactions in a Micro Fluidized Bed Reactor. *AIChE J.* 2010, 26, 2905–2912.

(29) Nyakuma, B.; Oladokun, O.; Bello, A. Combustion Kinetics of Petroleum Coke by Isoconversional Modelling. *Chem. Chem. Technol.* 2018, 12, 505–510.

(30) Zhang, Y.; Yao, M.; Sun, G.; Gao, S.; Xu, G. Characteristics and Kinetics of Coked Catalyst Regeneration via Steam Gasification in a Micro Fluidized Bed. *Ind. Eng. Chem. Res.* 2014, 53, 6316–6324.

(31) Jia, L.; Tan, Y.; Anthony, E. J. Emissions of SO2 and NOx during Oxy-Fuel CFB Combustion Tests in a Mini-Circulating Fluidized Bed Combustion Reactor. *Energy Fuels* 2010, 24, 910–915.

(32) Manoj, B.; Kunjomana, A. G. Study of Stacking Structure of Amorphous Carbon by X-Ray Diffraction Technique. *Int. J. Electrochem. Sci.* 2012, 7, 3127–3134.

(33) Sadikov, K.; Larionov, V.; Varfolomeev, M. In Evaluation Method of Influence of Catalyst Precursors on Initiation of In-Situ Combustion and It’s Dynamics, Society of Petroleum Engineers - SPE Russian Petroleum Technology Conference, 2017.

(34) Yuan, C.; Sadikov, K.; Varfolomeev, M.; Khalilullin, R.; Pu, W.; Al-Muntaser, A.; Saeed Mehraibi-Kalajahi, S. Low-Temperature Combustion Behavior of Crude Oils in Porous Media under Air Flow Condition for in-Situ Combustion (ISC) Process. *Fuel* 2020, 259, No. 116293.

(35) Kissinger, H. E. Reaction Kinetics in Differential Thermal Analysis. *Anal. Chem.* 1957, 29, 1702–1706.

(36) Ozawa, T. A New Method of Analyzing Thermogravimetric Data. *Bull. Chem. Soc. Jpn.* 1965, 38, 1881–1886.

(37) Flynn, J. H.; Wall, L. A. A Quick, Direct Method for the Determination of Activation Energy from Thermogravimetric Data. *J. Polym. Sci., Part B: Polym. Lett.* 1966, 4, 323–328.

(38) Mul, G.; Neef, J. P. A.; Makkee, M.; Kapteijn, F.; Moulijn, J. A. Catalytic Oxidation of Model Soot by Chlorine Based Catalysts. *Stud. Surf. Sci. Catal.* 1998, 116, 645–654.

(39) Mul, G.; Kapteijn, F.; Moulijn, J. A. Catalytic Oxidation of Model Soot by Metal Chlorides. *Appl. Catal., B* 1997, 12, 33–47.

(40) Young, B. C.; Smith, I. W. The Kinetics of Combustion of Petroleum Coke Particles at 1000 to 1800 K: The Reaction Order. *Symp. (Int.) Combust.* 1981, 18, 1249–1255.