

Isothermal decomposition and kinetic analysis of petroleum pitch in an inert atmosphere using the model-free method

Khokan Sahoo
Department of Aerospace
Engineering,
Indian Institute of Technology
Bombay, Maharashtra, India

Neeraj Kumbhakarna
Department of Mechanical
Engineering,
Indian Institute of Technology
Bombay, Maharashtra, India

Sudarshan Kumar
Department of Aerospace
Engineering,
Indian Institute of Technology
Bombay, Maharashtra, India

1 Introduction

The socioeconomic development of any country is closely related to the availability of energy resources. Electric power generation is one of the crucial factors in the economic growth of any country, and it is a critical factor for any developing country like India, which is at the peak of economic growth. The efficient use of available energy resources has become a scientific interest with rapid growth in power demand. However, the power generation from renewable energy resources increased significantly over the years to minimize environmental impacts and contributed generously to power generation worldwide [1].

Still, non-renewable source-based power generation is leading worldwide and will increase in the future to meet the power demand. Significantly coal-based power generation increases considerably per future predictions, placing coal as one of the fastest-growing power generations in the projection [2]. Currently, 57.5% of electricity generation in India is through fossil fuel-based resources, and the coal-based thermal power plant has the largest share at 49.7% [3]. The petroleum refinery by-product pitches are less expensive and readily available in large amounts. The calorific value of petroleum pitches is sufficient and Proper utilization of such materials as fuel can boost the revenue of the electricity generation and petroleum refining industries [4]. The amount of asphalt or pitch types of residue production is enormous from the crude oil refinery process; 0.92 gallons of asphalt is produced from one 42-gallon barrel of crude oil [5]. Petroleum crude oil refinery by-product pitches are challenging to handle from a combustion point of view because of their physical and chemical nature. Petroleum pitches are highly viscous, and the softening point is also relatively high; these characteristics create problems in atomization and fuel supply in a liquid state in a practical combustion scenario.

The petroleum pitches are by-products of crude oil refinery upgrading processes containing sulphur and heavy metals. Conventional incineration of such fuels always resulted in high levels of SO₂ emission and other environmental problems. A fluidized bed combustor (FBC) is always an alternative and a suitable option for the combustion of such petroleum pitches. Combustion of three heavy liquid fuels, pitch, tar, and bitumen, was studied in a pilot scale FBC combustor with a suitable fuel handling system ideal for supplying fuels, and promising combustion performance was reported [4]. Thermogravimetric analysis has been utilized as a fundamental method to understand the pyrolysis

behavior and corresponding kinetic scheme of various fossil fuels over the years. Pyrolysis is treated as the first step of the thermochemical transformation process. Detail understanding of thermochemical conversion processes and pyrolysis kinetic schemes have been used as a positive tool in process optimization and setting of industrial technology [6]. Solid-state reaction kinetics study has existed since the early 20th century. Several experimental techniques like thermogravimetry (TG), differential thermal analysis (DTA), and evolved gas analysis (EGA) were used as well-established practical techniques to study solid-state reaction kinetics, and initial stage all kinetics studies were conducted under isothermal conditions. There are several drawbacks to isothermal kinetic analysis; a fraction of thermochemical conversion is always achieved before reaching the desired isothermal kinetic temperature. This is not desirable in the case of a higher predetermined isothermal temperature. Conversely, a single non-isothermal experiment is sufficient to provide information about kinetic triplets (Activation energy, pre-exponential factor, mechanism function) and temperature dependence of reaction rate [7]. Despite several drawbacks, isothermal kinetic analysis was always considered because of its good establishment. Arrhenius parameters from non-isothermal conditions were expected to have a good agreement with the isothermal conditions but not the other way around. Some researchers reported good agreement between isothermal and non-isothermal Arrhenius parameters but, in some cases, found these to be inconsistent [7]. The theoretical explanation of the inconsistencies in isothermal and non-isothermal Arrhenius parameters was provided and found not to be a mandatory criterion in the kinetic analysis [8]. Solid-state reactions collectively refer to so many intermediate physical and chemical processes, including melting, adsorption, desorption, evaporation, diffusion, sublimation, solid-state decomposition, and the reaction of gaseous products with solid, polymorphous transitions, etc. The effective activation energy in a solid-state reaction is a collective representation of individual activation energy associated with all these complex processes to the overall reaction rate of a solid-state reaction. Therefore, the effective activation energy depends on temperature, even varying with the extent of conversion in an isothermal condition [9]. The model fitting cannot demonstrate the complexity associated with a solid-state reaction process because of displaying a single global Arrhenius parameter in isothermal and non-isothermal conditions. Flynn and Wall [7] first observed the variation of activation energy with the extent of reaction in a solid state reaction kinetics. The alternative model-free method based on the isoconversional approach can eliminate contradictions that arise in kinetic reaction model evaluation and demonstrate the variation of activation energy with the extent of the reaction. The complexity of the solid-state reaction and mechanistic conclusion can also be drawn through the isoconversional model-free approach in the isothermal and non-isothermal conditions [7].

Isothermal pyrolysis studies are essential because pyrolysis units are generally operated under isothermal conditions, and isothermal kinetic analysis helps design such reactors from the practical application point of view [10]. Cheng, Yan, et al. [6] investigated the pyrolysis behavior of deoiled asphaltenes, and two-stage thermal decomposition was reported. Kinetic parameters were evaluated from model-based prediction for the asphaltenes, and model-based prediction parameters were compared with experimental thermogravimetry results. Murugan, Pulikesi, et al. [11] studied the isothermal oxidation of coke derived from heating of Fosterton asphaltenes in a temperature interval of 25 °C between 375 and 500 °C. The kinetic parameters were evaluated from non-linear regression of isothermal combustion data. Ambalae, Aprameya, et al. [12] studied the isothermal oxidation of coke formed from whole oil and asphaltenes; isothermal experiments were fixed at 25 °C intervals for both cases, but the temperature ranges were 375 to 500 °C and 375 to 525 °C respectively. Kinetic parameters were evaluated based on linear regression and Arrhenius plot of isothermal combustion data. The activation energy of combustion of coke formed from asphaltenes and whole oil was 117.7 kJ/mol and 129.5 kJ/mol, respectively. The pre-exponential factors were 0.44×10^8 /min and 2.69×10^8 /min for coke derived from asphaltenes and whole oil, respectively. The current work aims to investigate the isothermal decomposition of petroleum pitch in an inert atmosphere through a model-free methodology based on an isoconversional approach.

2 Experimental procedure and Isothermal kinetics

Material

The material used for isothermal thermogravimetric analysis is the hydrocracked petroleum pitch. The vacuum residue from crude oil was used to produce hydrocracked petroleum pitch by a very complex process in the presence of the catalyst and hydrogen (H₂). The ultimate analysis of petroleum pitch is performed in a Flash smart v CHNS/O analyzer manufactured by ThermoFisher Scientific at the Sophisticated Analytical Instrument Facility, IIT Bombay (SAIF, IIT BOMBAY). The result of the elemental analysis is provided in Table 1, and other properties are mentioned in Table 2.

Table 1: Ultimate analysis (CHNSO)

Element	Mass (%)
Carbon (C)	78.821
Hydrogen (H)	6.046
Nitrogen (N)	1.178
Sulphur (S)	2.177
Oxygen (O)	0.775

Table 2: Properties of petroleum pitch.

Properties/Element	Value
Softening point	160-220 °C
Viscosity	1100 cSt at 60 °C.
Specific gravity	1.1-1.2
Calorific value	8500-900 Kcal/kg
Nickel	220 ppm
Vanadium	300 ppm
Volatile content	50%

Isothermal thermogravimetric analysis

Isothermal thermogravimetric analysis was conducted on a high-precision Shimadzu DTG-60 thermogravimetric analyzer. The petroleum pitch sample was sieved to a particle size of fewer than 250 µm and placed on an Aluminum crucible (6 mm dia and 3 mm height) under an inert Nitrogen (N₂) flow of 100 ml/min for all three isothermal temperatures of 439 °C, 463 °C, 488 °C. The initial heating rate was fixed at 60 °C/min to achieve an isothermal temperature in all three cases and placed up to 360 min, 350 min, and 320 min, respectively. Surface morphology and the presence of heavy metals (V, Ni) were studied on residue and a sample using scanning electron microscopy (SEM) imaging and energy dispersive spectrometer (EDS) mapping. ESEM FEI quanta 200 (3 mm resolution at 30 kV, magnification: 25x to 20,000x, accelerating voltage: 200 V to 30 kV, Vacuum modes: High vacuum, low vacuum, ESEM mode) at SAIF, IIT Bombay was used for SEM imaging and EDS mapping. The maximum time to attain isothermal temperature was within 449 S, and the weight losses to reach isothermal temperatures were 3.2%, 6.3%, and 8.4%, respectively. The sample weights were 5-6 mg for all three isothermal runs. The weight after achieving isothermal temperature is considered the initial weight, and the corresponding time is regarded as the initial time in calculating the extent of

the reaction or conversion (α) in the present isothermal kinetic analysis study. The extent of reaction or conversion (α) is defined as

$$\alpha = \frac{(W_{i,iso} - W_{t,iso})}{(W_{i,iso} - W_{f,iso})}$$

Where $W_{i,iso}$, $W_{f,iso}$, $W_{t,iso}$ are the initial, final, and instantaneous weight after achieving isothermal condition.

Isothermal Kinetics study

The kinetics studies are performed based on the below-mentioned kinetic equation. The reaction rate is generally defined with the following equation [7].

$$\frac{d\alpha}{dt} = f(\alpha)K(T) \quad (1)$$

Where $K(T)$ is the temperature-dependent rate constant, $f(\alpha)$ is the reaction mechanism function or kinetic scheme, α is the extent of reaction or conversion, t is the time, and T is the temperature, $\frac{d\alpha}{dt}$ is the reaction rate. By using Arrhenius's equation (1) can be written as follows:

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}}f(\alpha) \quad (2)$$

A is the pre-exponential factor, E is the activation energy, and R is the universal gas constant.

Equation (1) can be transformed as

$$g_j(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = K_j(T_i)t \quad (3)$$

Where j represents a particular reaction mechanism function or kinetic scheme, T_i denotes a specific temperature. The temperature-dependent rate constants are determined at different temperatures by the above equation (5), and the corresponding Arrhenius parameter can be evaluated by following the equation as

$$\ln(K_j(T_i)) = \ln A_j - \frac{E_j}{RT_i} \quad (4)$$

Under isothermal conditions, by combining equations (3) and (4), we can get the equation used for the isothermal model-free isoconversional approach as

$$\ln t_{\alpha,i} = \ln \left[\frac{g(\alpha)}{A} \right] + \frac{E_\alpha}{RT_i} \quad (5)$$

The slope of the plot of $\ln t_{\alpha,i}$ against $\frac{1}{T_i}$ is used for calculating activation energy (E_α) for a particular conversion [7,10].

3 Results and Discussion

The weight losses in isothermal decomposition for the temperatures of 439 °C, 463 °C, and 488 °C throughout the entire time were 36.37%, 37.89%, and 35.20%, respectively. There were no discernible differences in weight loss or conversion in the whole of the isothermal decomposition of petroleum pitch despite having different isothermal temperatures and holding periods, as shown in Figure 1 (Left), which represents the variation of conversion (α) with the time considered for the isothermal decomposition of petroleum pitch. A similar weight loss pattern was observed in the isothermal combustion of coke derived from Fosterton oil in the temperature range of 475- 500 °C [11]. Variation of Conversion (α) indirectly represents weight loss during isothermal decomposition, like a replica of

weight loss in the thermal decomposition process. The major of isothermal decomposition, nearly 70%, takes place within 278 S, which is very little, and the difference in time required to achieve 70% of the entire isothermal decomposition was negligible. A similar trend was found in the combustion of coke, as observed by Murugan, Pulikesi, et al. [11].

Evaluation of Activation energy and surface morphology.

A model-free methodology based on an isoconversional approach is used in the present study, and equation (5) is used to plot and obtain the linear fitting of isothermal decomposition data. The activation energy was determined from the slope obtained from the linear fitting equating with the (E/R) as shown in equation (5). The coefficient of determination (R^2) in linear fitting less than 0.8 is not considered after liner fitting, and the extent of reaction (α) up to 0.7 is satisfied, as shown in Figure 1 (Right).

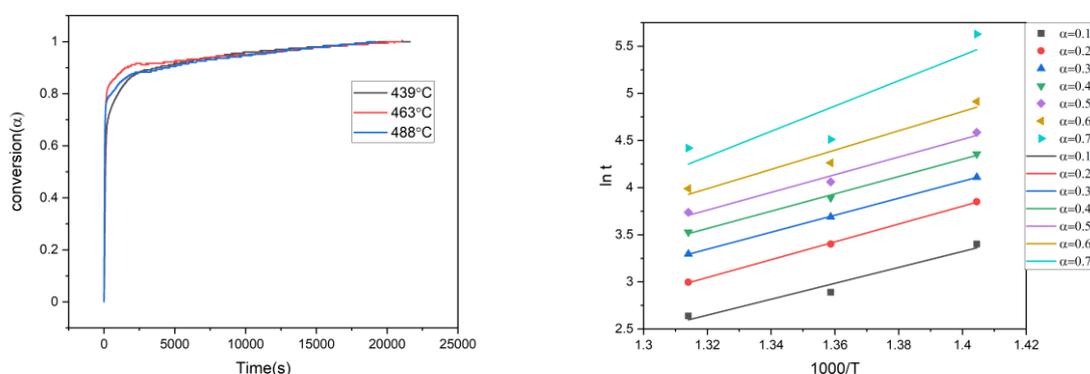


Figure 1: Isothermal kinetic plot of the petroleum pitch Left: The extent of reaction (α) of the pitch. Right: Liner fitting of isothermal model-free approach at various extents of reaction.

The activation energy variation was determined, as shown in Figure 2. Liu, Jianbiao, et al. [13] investigated the variation in activation energy with the extent of the reaction on an agricultural briquette within a particular extent of reaction (α) based on the criteria of coefficient of determination (R^2) obtained from liner fitting of isothermal decomposition data and a similar procedure was applied in the present study.

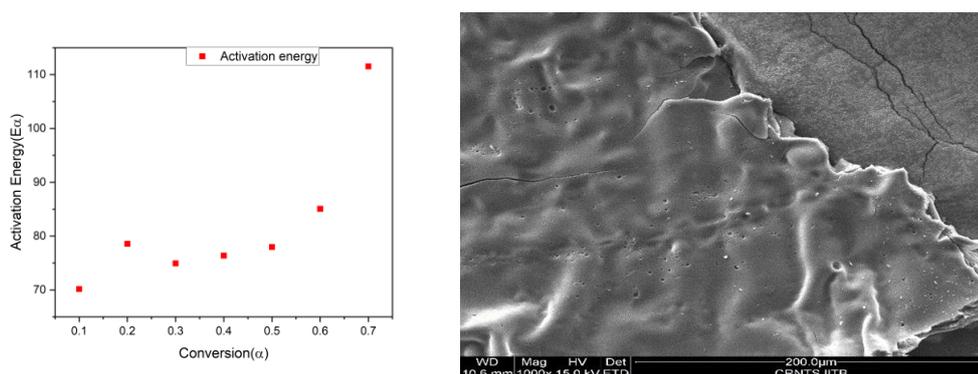


Figure 2: results of isothermal kinetic study Left: Activation energy vs. Conversion. Right: Surface morphology of residue after isothermal decomposition at 488 °C.

The isothermal decomposition fitted the model-free method well up to a conversion (α) of 0.7, and the activation energy variation was considerable. The minimum and maximum activation energies were 70.16 KJ/mol and 111.53 KJ/mol. The average activation energy was 82.086 KJ/mol for the extent of the reaction considered, as shown in Figure 2 (Left). This variation in activation energy

signifies the presence of complex processes like melting, thermal decomposition, and softening of petroleum pitch during the isothermal decomposition of petroleum pitch in an inert atmosphere. The proliferation of numerous tiny pores and some fissures were visible on the surface morphology of residue after isothermal decomposition at 488 °C, as shown in Figure 2 (Right). The tiny pores are formed from releasing large gaseous volatiles during thermal decomposition, and the fissure signifies the condensation reaction of macromolecular structures. The amount of vanadium and Nickel at a similar residue was 1.1% and 0.6%, respectively, which can create problems in practical applications. Shi, H, et al. [14] found similar surface morphology and chemical elemental analysis results on the asphaltene combustion residue.

4 Conclusions

The variation of activation energy with conversion was considerable in the isothermal thermal decomposition of petroleum pitch, and the existence of intermediate complex processes was confirmed. The average activation energy was 82.086 KJ/mol for the best-fitted range of conversion (α) up to 0.7. The model-free method for isothermal decomposition of petroleum pitch-based isoconversional approach suited well. Some amount of Vanadium (V) and Nickel (Ni) is present in the residue.

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