

Article

A Thermal Study on Peat Oxidation Behavior in the Presence of an Iron-Based Catalyst

Mohammed A. Khelkhal ^{1,*}, Semen E. Lapuk ¹, Nikita E. Ignashev ¹, Alexey A. Eskin ¹, Mikhail Yu. Glyavin ², Nikolay Yu. Peskov ², Tatiana O. Krapivnitskaia ² and Alexey V. Vakhin ¹

¹ Department of Petroleum Engineering, Kazan Federal University, Kremlevskaya str. 18, 420008 Kazan, Russia; lapuksemen@gmail.com (S.E.L.); Ignashev13nik@mail.ru (N.E.I.); eskin.aleksey@gmail.com (A.A.E.); vahin-a_v@mail.ru (A.V.V.)

² Institute of Applied Physics, Russian Academy of Sciences, 46 Ulyanova st., 603950 Nizhniy Novgorod, Russia; glyavin@appl.sci-nnov.ru (M.Y.G.); peskov@appl.sci-nnov.ru (N.Y.P.); kto465@yandex.ru (T.O.K.)

* Correspondence: amine.khelkhal@gmail.com; Tel.: +7-(986)-916-39-12

Abstract: Peat is a resource used for heat and energy, particularly in countries where peat is abundant and conventional fuels are not available. Some countries have made extensive use of peat resources to produce electricity and heat in addition to light hydrocarbons. By doing so, they were able to reduce the cost of importing fossil fuels. To the best of our knowledge, there is a lack of a detailed description of the peat oxidation process in the presence of other substances. Herein, the process of peat oxidation was studied in-depth by means of thermal analysis in the presence of iron tallate acting as a catalytic agent. Differential scanning calorimetry and thermogravimetric analysis demonstrated an oil-like oxidation behavior during the combustion of the used peat. The process of peat oxidation includes two main regions: low-temperature oxidation (LTO), which occurs during the oxidation of light hydrocarbons, followed by the so-called high-temperature oxidation (HTO), which includes the oxidation of the obtained coke-like product. Moreover, the application of non-isothermal kinetics experiments based on the isoconversional and model approach principle have confirmed the role of 2% iron tallate in peat mass by improving the oxidation rate at low- and high-temperature oxidation (HTO) regions. The results obtained from this study have proven that the added catalyst improves efficiency with regards to the energy activation in the process by leading to its significant decrease from 110.8 ± 7.8 kJ/mol to 81.8 ± 7.5 kJ/mol for LTO and from 157.8 ± 19.1 kJ/mol to 137.6 ± 9.3 kJ/mol for HTO. These findings clearly confirm the improvement in the rate of the process by shifting the LTO and HTO peaks to lower regions in the presence of the catalyst. These results further emphasize the possible impact which could be generated by the application of thermally enhanced oil recovery methods on peat development and exploitation.

Keywords: unconventional resources; peat; oxidation; thermal analysis; catalysts; iron oxide nanoparticles; DSC; TG; non-isothermal kinetics



Citation: Khelkhal, M.A.; Lapuk, S.E.; Ignashev, N.E.; Eskin, A.A.; Glyavin, M.Y.; Peskov, N.Y.; Krapivnitskaia, T.O.; Vakhin, A.V. A Thermal Study on Peat Oxidation Behavior in the Presence of an Iron-Based Catalyst. *Catalysts* **2021**, *11*, 1344. <https://doi.org/10.3390/catal11111344>

Academic Editors: Jingbo Jia and Haiming Wang

Received: 12 October 2021

Accepted: 6 November 2021

Published: 9 November 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Peat is among the most commonly discussed types of fossil fuel alternatives for improving the world's production of hydrocarbons and fuels due to the shortage of unconventional hydrocarbon reserves [1–6]. Furthermore, the last two decades have witnessed a huge growth in fossil fuel demand and consumption which has resulted in insufficient supply from the oil market. In order to face the issues resulting from fossil fuel use and shortages, alternative energy sources such as peat are of particular importance [7–10]. Although researchers have widely shown interest in peat production and exploitation, there is still much work to be carried out regarding the mechanism of peat thermal degradation and energy transfer from these resources [11,12]. Tons of peat mass is produced annually from different marine and urban solid wastes, and yet, the mechanism of peat combustion has

been poorly studied. Industry, agriculture, and forests are, therefore, decaying, resulting in environmental problems and toxic gas emissions [13,14].

Peat is used in different sectors, such as medium-scale combined heat and power plants, which generate electricity and heat for industrial processes [15–17]. Moreover, peat represents a potential source of hydrocarbons that can be extracted by applying methods to enhance oil recovery. Enhancing oil recovery (EOR) methods is attracting considerable interest in the petroleum scientific community which deals with the different sources of energy exploitation. EOR consists of a set of methods that could be applied for recovering hydrocarbons from unconventional resources [18]. EOR is classified into chemical [19,20], physical [21,22], and thermal methods [23,24] depending on the applied technique. Among these methods, thermal enhanced oil recovery methods are attracting great interest in terms of recovery and economy. Perhaps the most attractive method is in situ combustion. It is based mainly on burning a part of the hydrocarbons in order to generate additional heating into the reaction medium due to exothermic reactions associated with the process of oxidation [25]. Today, the commonly accepted model for in situ oxidation consists of three main regions which are known as LTO, the fuel deposition region, and HTO [26,27]. The LTO region leads to the formation of oxygenated hydrocarbons as a result of oxygen combined with the oil components. The fuel deposition step transforms the obtained oxygenated hydrocarbons into gas hydrocarbons and coke-like products. Finally, the HTO, which is believed to be the key element for a successful application of in situ combustion, leads to the oxidation of the obtained coke-like product and releasing a high amount of heat due to the exothermic nature of the process [28]. Regardless of the promising perspectives expected from the application of in situ combustion for EOR from oil reservoirs, or enhancing hydrocarbon generation in industrial plants from peat, this method is still suffering from a lack of kinetic and thermodynamic studies which mostly leads to its unsuccessful application [29]. However, an increasing number of recent works have reported that the use of catalysts may result in the successful application of the latter [30–32]. In our previous works, we have studied the effect of different oil-soluble catalysts [33,34], in addition to the effect of manganese oxide nanoparticles [35], on the heavy oil oxidation process by means of thermal analysis. It has been found that the use of a catalyst decreases the activation energy in the process, especially in the HTO region. Therefore, the novelty of the present work lies in the use of different catalysts for improving the kinetics of oxidation reactions of peat which may lead to better hydrocarbon content. In the present study, the oxidation kinetics behavior of peat in the absence and the presence of iron tallate catalysts was investigated in order to highlight the process features for further study and application by differential scanning calorimetry and thermogravimetric analysis.

2. Results

2.1. Experimental

2.1.1. Materials

To study the characteristics of peat oxidation, a sample of high-quality peat with a low degree of decomposition (less than 65% humidity, more than 90% organic matter content, less than 10% ash content, and an acidity of 2.5%) was been obtained from the Greko-Ushakovskoye field. The obtained peat comprised a complex chemical composition (Table 1) which was determined by the conditions of genesis, the variety of peat-forming plants, and the degree of decomposition. Iron tallate was synthesized by using a set of organic solvents (purer than 99.5%), which were obtained from Component Reactive and used without additional purification. Moreover, the used inorganic salts were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Table 1. The main components contained in the Greko-Ushakovskoye field peat.

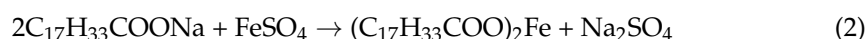
Component Composition of Peat Organic Matter	Mass Fraction in the Composition, %
Cellulose	4–10
Humic acids	15–50
Lignin	5–20
Easily hydrolyzable compounds	20–40
Water-soluble substances	1–5

2.1.2. Iron Tallate Preparation

The synthesis of the iron tallate catalyst was performed according to a well-known procedure [36]. The distilled tall oil (DTO) was used as a precursor, which resulted in iron carboxylate by inorganic iron salt exchange reactions with DTO sodium salt. The procedure had two main steps starting with saponification of fatty acid as follows:



The next step was to include the carboxylate interaction with iron sulfate at a higher temperature as follows:



To investigate the process of peat oxidation, 2 wt% of iron tallate was mixed with a peat sample and then used in thermal analysis experiments.

2.1.3. Thermal Analysis

The STA 449 F1 Jupiter (Netzsch) thermoanalyzer was adopted for investigating the oxidation process of peat by means of differential scanning calorimetry (DSC) and thermogravimetric (TGA) analyses at a temperature range from 30–600 °C with a heating rate of 5, 10, 15, 20 °C × min^{−1} and 50 mL × min^{−1} airflow. The Proteus Analysis v5.2.1, NETZSCH Peak Separation (version 2010.09), and NETZSCH Thermokinetics 3.1 (version 06.08.2014) program package was used for obtaining data.

The heterogeneous oxidation processes are considered complex and hard to study because of the nature of the reaction medium, which contains the gaseous, liquid, and solid states, and the occurrence of diffusion processes that should be considered as well. Therefore, many experts in the field of heterogeneous kinetics recommend describing the kinetics of such processes in their function of conversion degree and oxygen partial pressure as:

$$\frac{d\alpha}{dt} = k(T)P_{\text{O}_2}^a(1 - \alpha)^b \quad (3)$$

where α is the conversion degree and could be calculated by differential scanning calorimetric and thermogravimetric data, b is the reaction order, and P_{O_2} is the oxygen partial pressure. The rate constant $k(T)$ is expressed by Arrhenius law as presented by Equation (4):

$$k(T) = Ae^{-\frac{E}{RT}} \quad (4)$$

For the sake of simplicity, the process of peat oxidation was approached in the same way as oil oxidation due to the similar nature of both substances which mainly consists of hydrocarbons. Hence, the oil oxidation reaction order was assumed to be equal to 1 relative to oil concentration and oxygen partial pressure [37,38]. In addition, the oxygen partial pressure was considered constant during DSC/TG analysis since the thermal analysis was based mainly on small samples sizes and they were provided in a large furnace with high airflow. Thus, Equation (3) transforms into:

$$\frac{d\alpha}{dt} = k_{eff}(1 - \alpha) \quad , \quad \text{where } k_{eff} = kP_{\text{O}_2} \quad (5)$$

2.1.4. Kinetic Analysis

The aim of the present study was to reveal the oxidation behavior of peat from a kinetic analysis perspective. Consequently, the isoconversional and model approaches of non-isothermal kinetics [39,40], in addition to the Kissinger method [41], were selected to study the kinetic behavior of the peat oxidation process as recommended by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) [39].

The isoconversional principle is based on the idea that the reaction rate is only a function of temperature at a constant conversion. Therefore, in this study we chose Kissinger's method (ASTM E2890) [42], Friedman's analysis [43], and the Kissinger–Akahira–Sunose method for finding out the kinetic parameters of peat oxidation.

To choose the model associated with the oxidation of peat we adopted the approach of minimizing the difference between the experimentally measured and calculated data on the reaction rate [39]. The models used during the process of approaching a model are presented in Table 2. Moreover, the prediction of conversion times at different degrees of conversion [44,45] led to the evaluation of the catalyst's efficiency on the process of peat oxidation.

Table 2. Model methods for calculating kinetic parameters.

Model.	Equation
Reaction of n^{th} order (Fn)	$f = (1 - \alpha)^n$
Two-dimensional phase boundary (R2)	$f = 2(1 - \alpha)^{1/2}$
Three-dimensional phase boundary (R3)	$f = 3(1 - \alpha)^{2/3}$
N-dimensional nucleation according to Avrami-Erofeev (An)	$f = n \cdot (1 - \alpha) \cdot [-\ln(1 - \alpha)]^{(n-1)/n}$
Expanded Prout–Tompkins equation (Bna)	$f = (1 - \alpha)^n \cdot \alpha^{\text{AutocatOrder}}$
Reaction of n^{th} order with m-Power autocatalysis by product (Cnm)	$f = (1 - \alpha)^n \cdot (1 + \text{AutocatOrder} \cdot \alpha^m)$

2.2. Discussion

2.2.1. Thermal Analysis

Thermal analysis has beneficial applications in studying thermal degradation processes such as peat oxidation. Moreover, this analysis has a more practical solution for studying hydrocarbon oxidation processes in terms of its simplicity, being less time-consuming, and costing less. The changes in peat oxidation behavior were identified using thermogravimetric analysis in correlation with differential scanning calorimetry. The thermogravimetric results obtained at different heating rates in addition to their differential data are illustrated in Figure 1.

The thermogravimetric and differential thermogravimetric analysis curves highlight that the process of peat oxidation includes two main stages as illustrated by the three-step character of mass loss in thermogravimetric curves in the presence and the absence of the catalyst. Moreover, there was a significant correlation between thermogravimetric and differential thermogravimetric curves regarding these zones of the oxidation process. Both data exhibit two main peaks at each heating rate as shown on both curves. The aforementioned zones are well-studied in the literature and are generally described to be the LTO region (250–350 °C) and the HTO region (390–500 °C). Previous studies of the peat oxidation process have been limited by the choice of the appropriate methods allowing a detailed description of its oxidation mechanism and the rate at which it occurs. Moreover, these studies have failed to consider the impact of applying transition metal-based catalysts to improve the process of peat oxidation. However, the thermogravimetric results obtained during this study proved the impact of iron tallate as an effective catalyst in the process of peat oxidation as it led to peak temperature shifting of the LTO and HTO regions as shown in Figure 1 and illustrated by Figure 2.

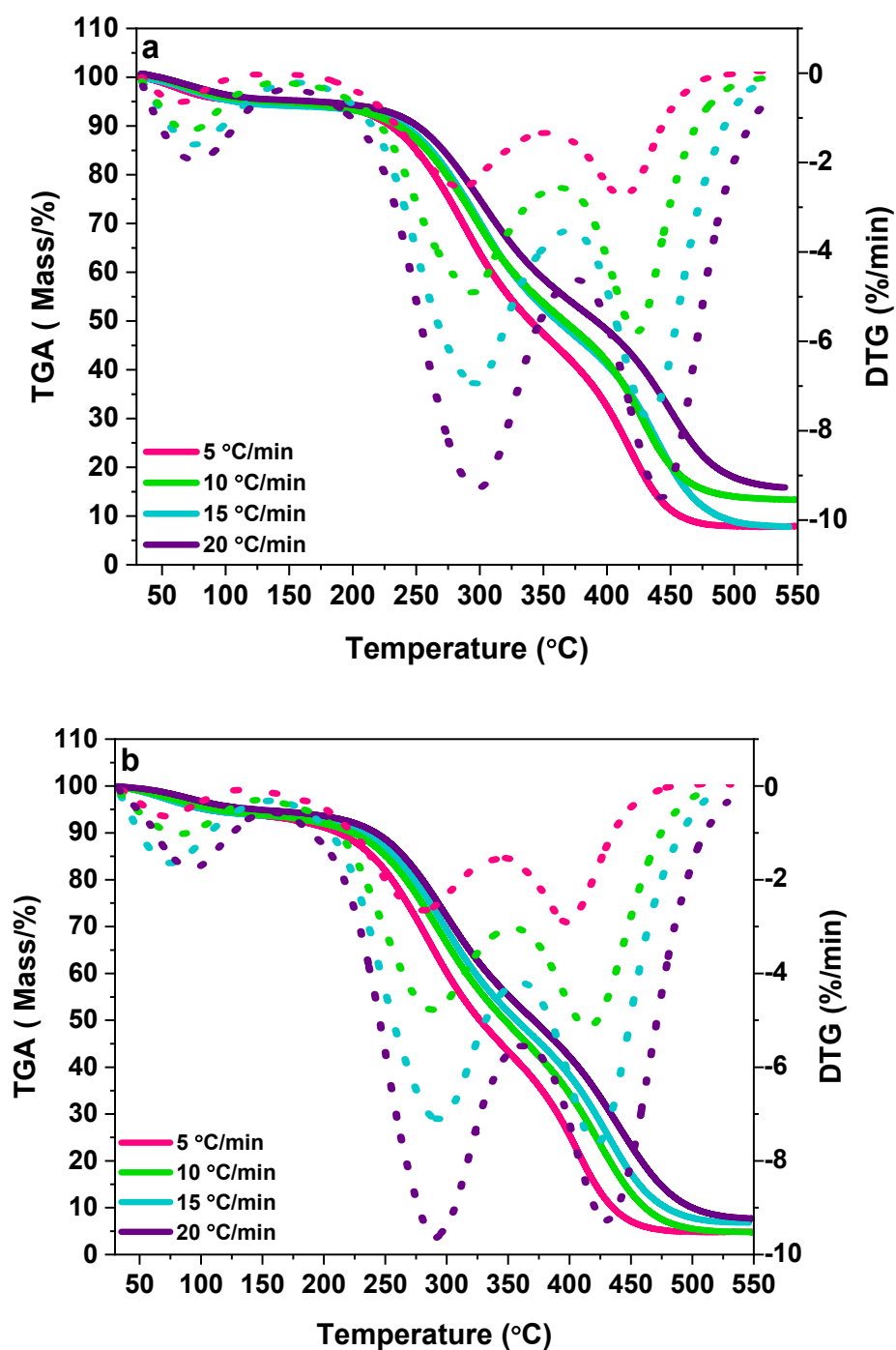


Figure 1. Thermal gravimetric and differential thermal gravimetric curves of the non-catalytic (a) and catalytic (b) processes of peat oxidation.

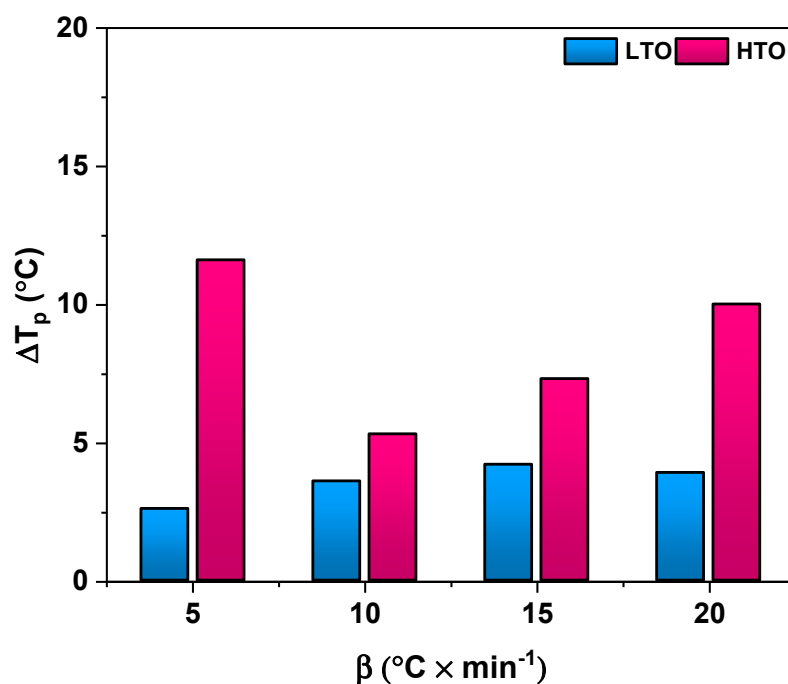


Figure 2. Differences between the peak temperatures (ΔT_p) of non-catalytic and catalytic peat oxidation for LTO and HTO regions at different heating rates obtained from thermogravimetric and differential thermogravimetric analysis.

As well as thermogravimetric and differential thermogravimetric analysis, differential scanning calorimetric (DSC) study confirmed the observed effect of the use of the catalyst in decreasing the temperature at which the process of the LTO and HTO of the studied peat occurs (Figure 3).

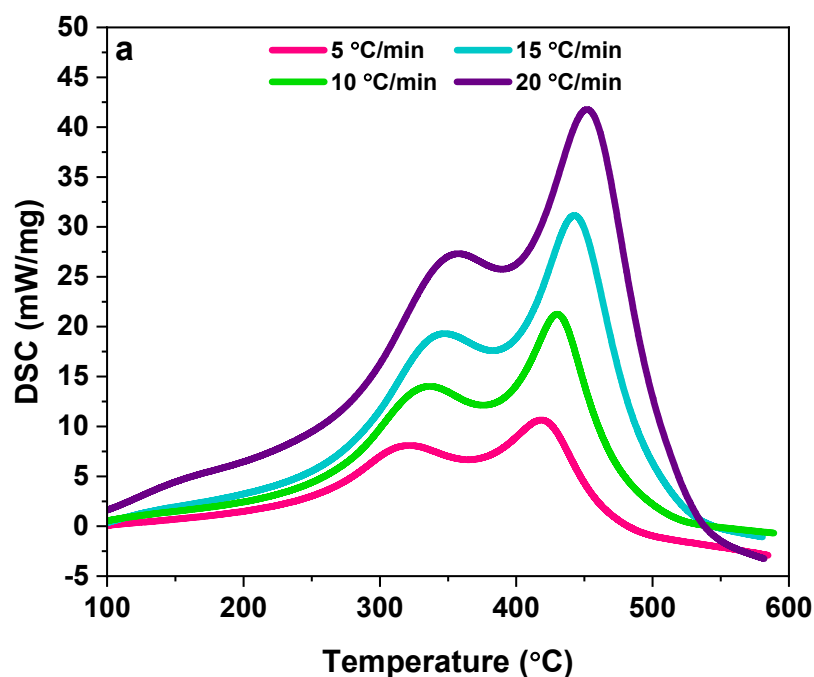


Figure 3. Cont.

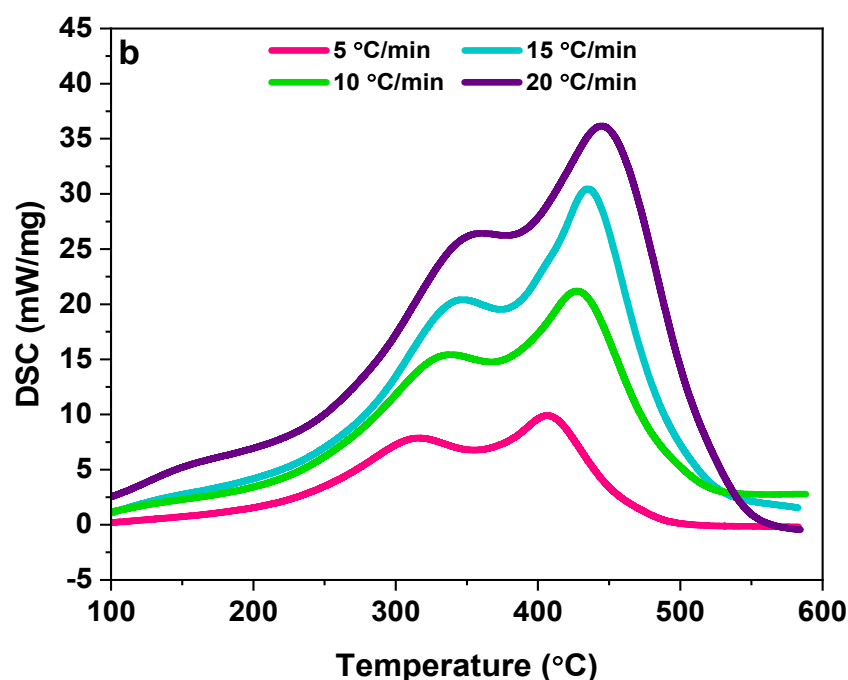


Figure 3. DSC curves for non-catalytic (a) and catalytic (b) peat oxidation.

The most striking results that emerged from the DSC data were the presence of two main peaks and the influence of the catalyst presence in the process of oxidation. In other words, Figure 3 highlights two main oxidation regions related to the LTO and HTO processes. In addition, the catalyst adopted for this study improved the process rate by shifting the peak temperatures at which the reactions of LTO and HTO occurred in the lower regions. In order to confirm the impact generated by the addition of the catalyst in the process, the difference in peak temperature shifts from the obtained DSC data was calculated as illustrated in Figure 4.

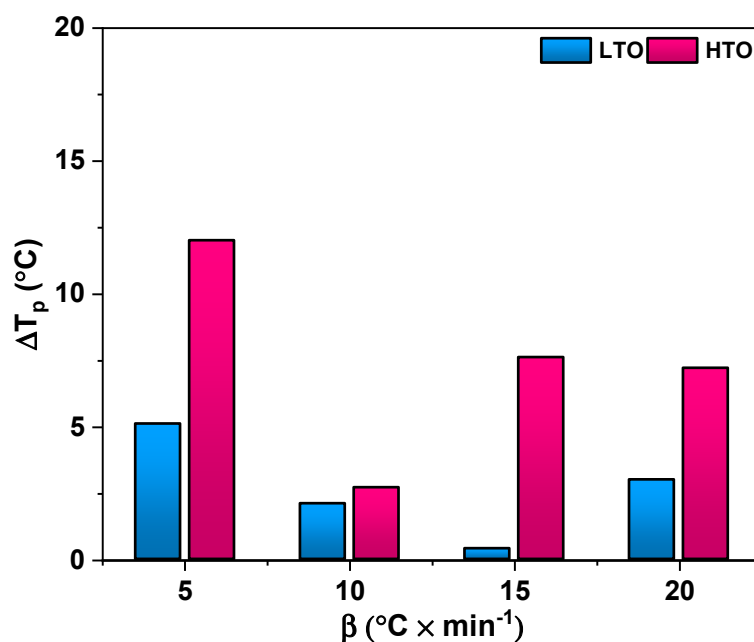


Figure 4. Differences between the peak temperatures (ΔT_p) of non-catalytic and catalytic peat oxidation for low- and high-temperature regions at different heating rates obtained from differential scanning calorimetric data.

Broadly speaking we found a significant correlation between thermogravimetric, differential thermogravimetric analysis, and differential scanning calorimetric results, which point toward the efficiency of the catalyst on the peat oxidation process by decreasing the peak temperature shifts at different heating rates. Interestingly, the obtained data show an oil-like oxidation behavior for peat. These results have further strengthened our hypothesis about the possibility of peat development and exploitation via thermally enhanced oil recovery methods such as in situ combustion. Given that our results are based only on a simple observation of thermal analysis data which led to highlighting the oil-like oxidation behavior of the peat oxidation process, we should, thus, further use these data to describe the kinetic aspect of the associated process for the in-depth study of the energy of activation for each step of oxidation.

2.2.2. Kinetic Study

In order to confirm the results of thermal analysis, the isoconversional and model approach principle was applied for calculating the kinetic parameters of the processes of peat oxidation in the presence and the absence of iron tallowate. Figure 5 shows the Kissinger curves which allow for calculating the energy of activation and the pre-exponential factor associated with the LTO and HTO of peat in the presence and the absence of the iron tallowate catalyst. The energy of activation and the pre-exponential factor obtained by Kissinger's method for each oxidation region are classified in Table 3.

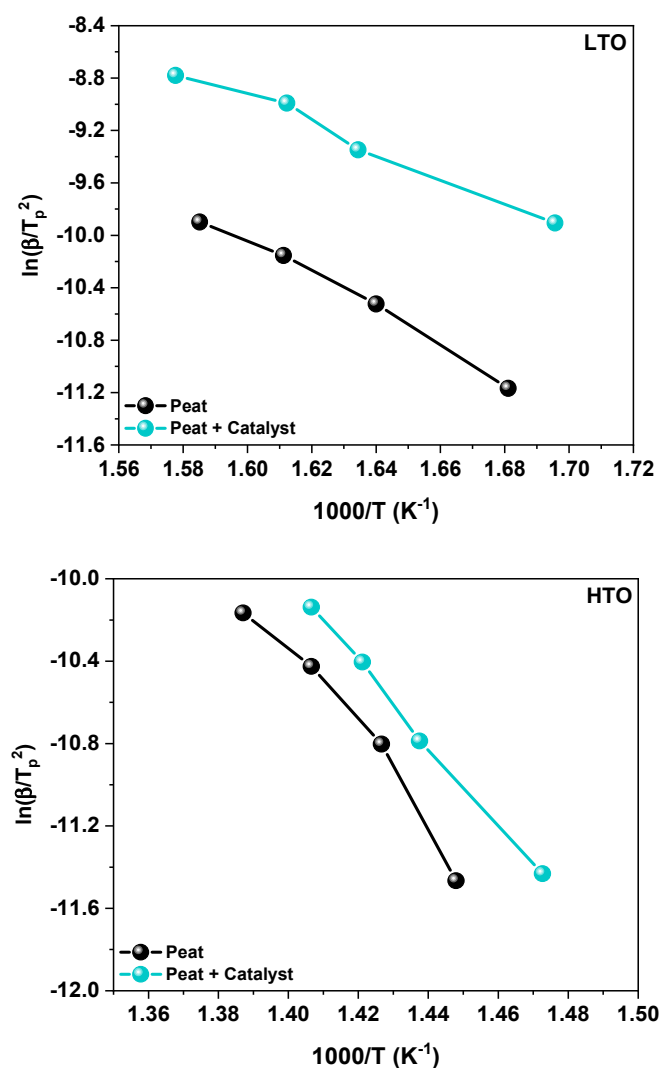
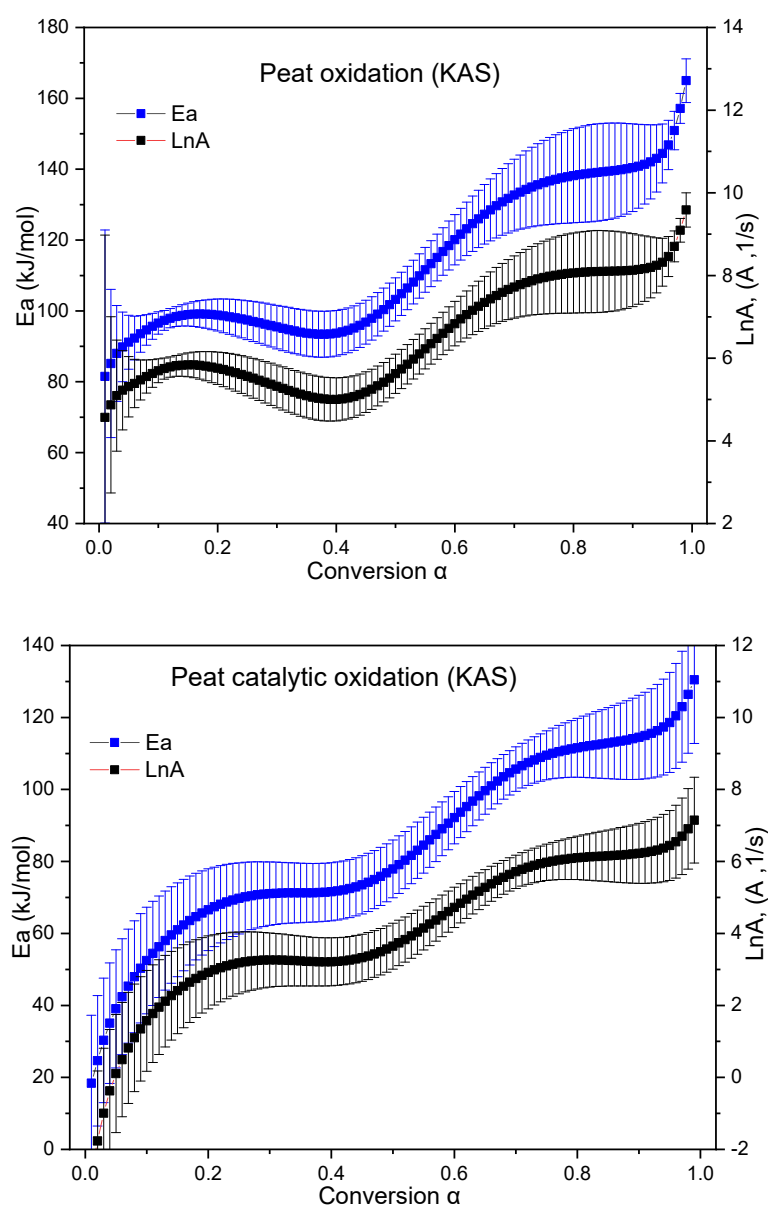


Figure 5. Kissinger's plots for catalytic and non-catalytic peat oxidation.

Table 3. Kinetic parameters of peat oxidation processes.

	Non-Catalytic		Catalytic	
	LTO	HTO	LTO	HTO
E_a , kJ/mol	110.8 ± 7.8	157.8 ± 19.1	81.8 ± 7.5	137.6 ± 9.3
$\log_{10} A$, A in min^{-1}	11.2 ± 1.53	16.0 ± 3.2	6.7 ± 1.47	12.9 ± 1.6

Furthermore, we applied the KAS and Friedman methods to understand the behavior associated with peat oxidation in the presence and absence of iron tallate. Activation energy dependency on the conversion degree is used as a reliable tool to explain the different phases of the peat oxidation path. Figure 6 shows the peat oxidation energies of activation at different conversion degrees.

**Figure 6.** Cont.

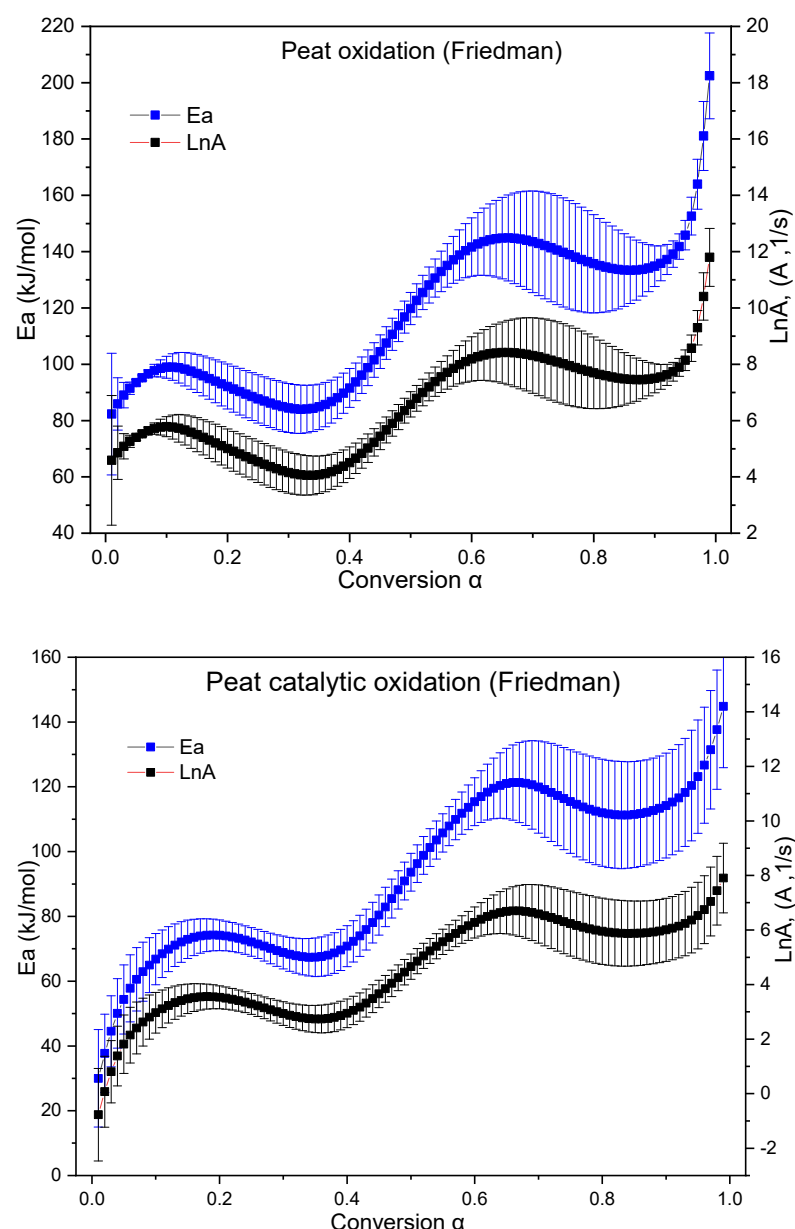


Figure 6. Peat oxidation activation energy dependency on conversion degree in the presence and absence of iron tallate obtained by the Friedman and KAS method.

Figure 6 indicates a significant variation in activation energy values at different conversion degrees with the presence of the so-called “shoulder” which witnesses the multistep nature of the peat oxidation process either in the presence of iron tallate or in its absence. The obtained curves are quite similar to those obtained in the literature for the process of heavy oil oxidation. Likely, the two main regions present in the obtained shoulder of each curve for both the catalytic and non-catalytic oxidation of peat are associated with the LTO and HTO regions. These regions generally describe the process of the heavy oil in the in situ oxidation process where LTO includes the formation of oxygenated compounds such as alcohols, aldehydes, and ketones. Meanwhile, HTO refers to the oxidation of the obtained coke-like product from the previous stage (LTO).

Broadly speaking, experts in the field of heterogeneous catalysis recommend the use of the model approach to confirm the obtained data by the isoconversional approach for estimating the effective reaction rates in both LTO and HTO, and, thereby, the effect of catalysts on these oxidation regions. For this reason, we have applied the model approach on LTO and HTO to assess the effect of iron tallate on these oxidation regions. The model

processing was established by selecting 32 two-step models for each stage of peat oxidation in the presence and absence of iron tallate. So that we would be able to select the adequate model we have referred to the aforementioned modes in Table 2. Moreover, the selection of the optimal model for the processes of peat oxidation was performed by means of the F-test [46]. Table 4 shows the models obtained by the application of the F-test value of 1.000. A detailed consideration of each of the calculated models is presented in (Supplementary Materials Table S1). Figure 7 presents the DSC curves of the obtained peat oxidation models in the absence and presence of the catalyst.

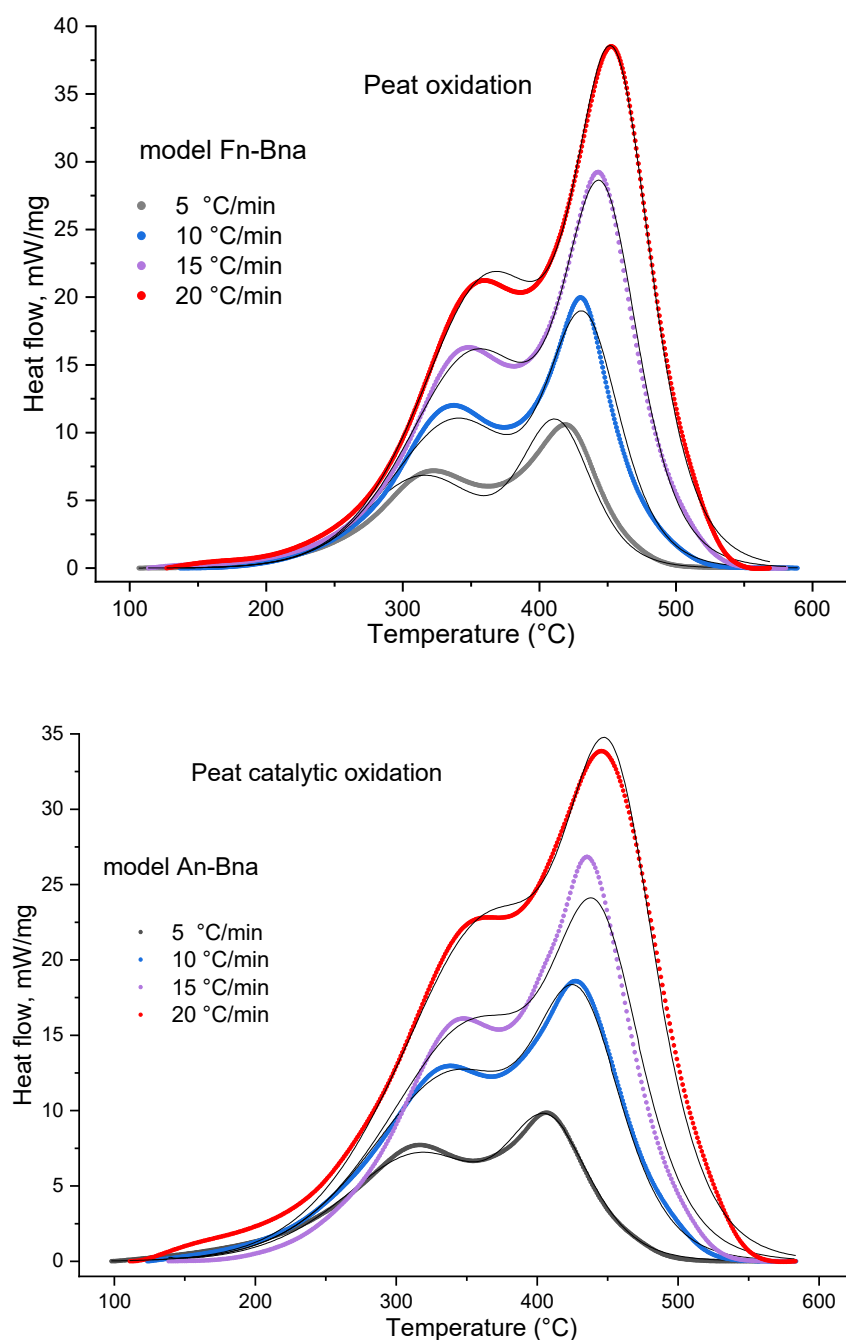


Figure 7. DSC model curves of peat oxidation in the presence and absence of iron tallate.

Table 4. Kinetic parameters of peat model oxidation processes.

Models Please indicate LTO and HTO	Peat Catalytic Oxidation	Peat Oxidation
	An: $E_a = 75.8 \text{ kJ}\cdot\text{mole}^{-1}$, $\text{LgA} = 4.1 \text{ s}^{-1}$, Dimension $n = 0.78$ Bna: $E = 116 \text{ kJ}\cdot\text{mole}^{-1}$, $\text{LgA} = 6.4 \text{ s}^{-1}$, ReactOrder $n = 1.51$, AutocatOrder 0.206	Fn: $E_a = 76.3 \text{ kJ}\cdot\text{mole}^{-1}$, $\text{LgA} = 4.1 \text{ s}^{-1}$, ReactOrder $n = 1.45$ Bna: $E = 132.2 \text{ kJ}\cdot\text{mole}^{-1}$, $\text{LgA} = 7.7 \text{ s}^{-1}$, ReactOrder $n = 1.48$, AutocatOrder 0.254
R^2	0.99715	0.99833
F-test	1.000	1.000

The obtained models were established as autocatalytic reactions of type: An for the catalytic LTO of peat; Fn for the non-catalytic LTO of peat; Bna for the catalytic and non-catalytic HTO. The selected models demonstrated the same behavior of kinetic parameters as in the case of the isoconversional approach results and Kissinger method data. In other words, the obtained models witnessed a slight decrease in the activation energy in the LTO while manifesting a significant decrease in activation energy in the HTO; this reflects the effect of the adopted catalyst in this region which is widely believed to be the key to a successful application of in situ oxidation.

3. Peat Oxidation Rate Constant Calculation

As expected from TG/DSC curves, there was strong evidence from the obtained kinetic parameters about the impact of using a catalytic agent such as iron tallate for improving the LTO and HTO of peat. The obtained results highlight a decrease in energy of activation in the presence of the catalyst from 110.8 to 81.8 kJ/mol (for LTO) and from 157.8 to 137.6 kJ/mol (for HTO). In our view, these results emphasize the validity of the adopted catalyst in improving the peat oxidation process. However, the obtained pre-exponential factor values for the LTO and HTO of peat demonstrated an opposite effect of the adopted catalyst. The pre-exponential factor values decreased in the presence of the catalyst from 11.2 to 6.7 min^{-1} (for LTO) and from 16 to 12.9 min^{-1} (for HTO). Taken as a whole, the energy of activation and pre-exponential factors demonstrated a noticeable disagreement about the effect of iron tallate on the process of peat oxidation. The energy of activation and the pre-exponential factor were inversely proportional to the effective reaction rate expressed by the Arrhenius equation. Therefore, to evaluate the total effect of these two parameters on the peat oxidation process in the presence and absence of iron tallate, we calculated the effective oxidation rate constants within a large temperature range where these processes occur. The effective reaction rate constants of the LTO and HTO of peat are provided in Figure 8.

Figure 6 shows higher effective rate constants in both regions for the LTO and HTO processes in the presence of iron tallate compared to the non-catalytic processes. It is fundamental to note that the influence of the catalyst is obvious especially in the LTO region, which generates oxygenated compounds through partial oxidation. The correlation between TG/DSC data and the obtained kinetic results is noteworthy because it reveals the importance of the catalyst's role in enhancing the peat oxidation process, especially in generating oxygenated compounds and hydrocarbon as a promising alternative source of biofuels. Although our investigations so far have only been on a small scale, we still believe that iron tallate exhibits different oxidation states during the peat oxidation process and it transforms into iron oxide nanoparticles at higher temperatures. These nanoparticles possess a strong catalytic effect on the process of peat oxidation due to a higher surface area due to the adsorption of the generated hydrocarbon from peat on its surface, and, thus, performing the catalytic action in a short time. Our findings and hypotheses appear to be well-supported by our previous work on heavy oil oxidation [33–35]. We are aware

that our research may contain limitations, such as the lack of other physical methods for confirming our hypotheses about catalyst transformation during the peat oxidation process. Nevertheless, to the best of our knowledge, we believe that there is limited study on non-isothermal kinetics for such a valuable alternative source of energy as peat. The present work could be used to generate the interest of other researchers to undertake investigations into peat in future research.

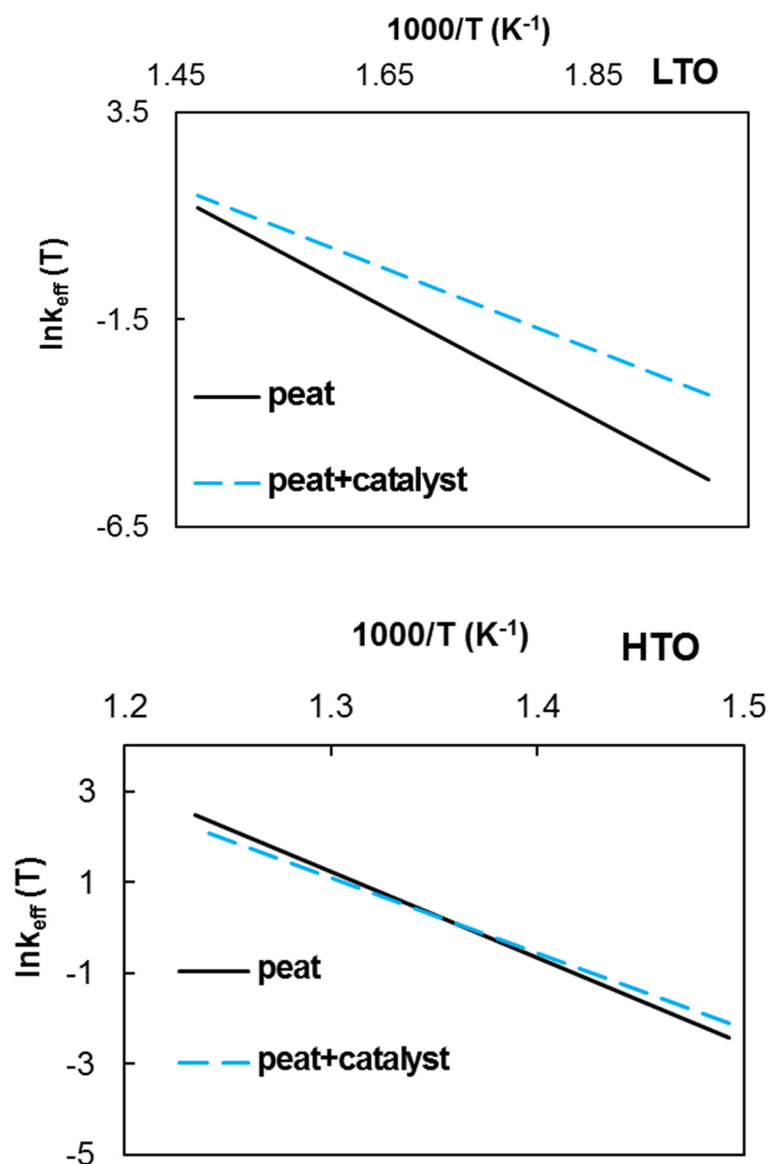


Figure 8. Variation of effective reaction rate constants with temperature for catalytic and non-catalytic peat oxidation.

4. Kinetic Predictions

It is worthy to note that the model approach values obtained for the pre-exponential factor followed the same pattern of change as those values obtained by means of the isoconversional principle or by the Kissinger method. The pre-exponential factor values decreased in the presence of iron tallate, which may have affected the overall reaction rate since the pre-exponential factor and activation energy were inversely proportional to the reaction rate according to the Arrhenius equation.

Therefore, to evaluate the total effect of these two parameters on the peat oxidation process in the presence and absence of iron tallate, we calculated the oil conversion time

versus temperature for different degrees of conversion (Figure 9) using the models obtained from Table 4. The calculated oxidation times of peat in the presence and absence of catalysts at 10%, 50%, and 90% oxidation conversion are presented in Figure 9.

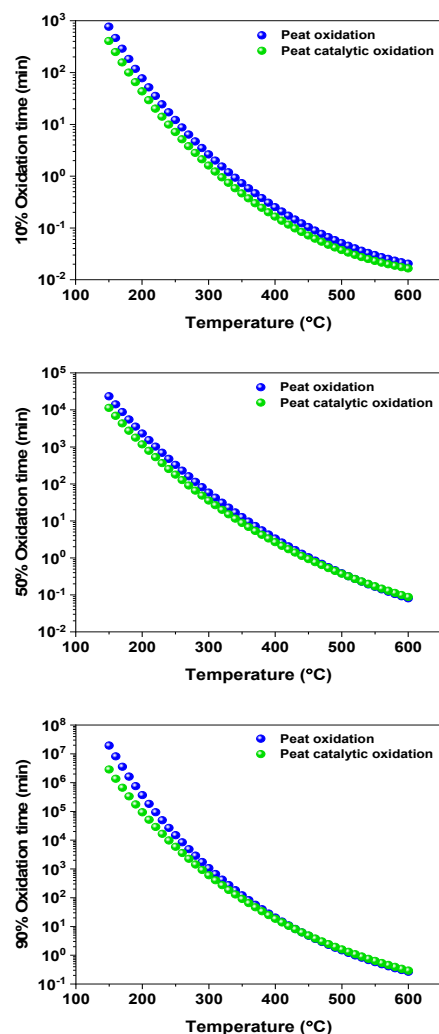


Figure 9. Calculated oxidation times of peat in the presence and absence of catalysts at 10%, 50%, and 90% oxidation conversions.

Figure 9 shows less conversion time in both regions at the LTO and HTO processes in the presence of iron tallate compared to non-catalytic processes which witness a high reaction rate in the presence of iron tallate. It is fundamental to note that the influence of the catalyst is obvious especially in the HTO region, which is considered the main region for a higher generation of a combustion front, which, consequently, leads to the pyrolysis of the adjacent amount of peat, and, which, in turn, releases light hydrocarbons and gases. The correlation between TG/DSC data and the obtained kinetic results is noteworthy because it revealed the importance of the catalyst's role in enhancing the peat oxidation process, especially in generating the considerable amount of needed heat on large scales for improving hydrocarbon generation from such potential resources like peat. Although our investigations so far have been on a small scale, we still believe that iron tallate exhibits different oxidation states during the peat oxidation process and it transforms into iron oxide nanoparticles at higher temperatures. These nanoparticles possess a strong catalytic effect on the process of peat oxidation due to higher surface area due to the adsorption of the generated hydrocarbons from peat on its surface, and, thus, performing the catalytic action in a short time on the resulting coke. Our findings and hypotheses appear to be well-supported by our previous works on heavy oil oxidation [33–35]. We are aware that

our research contains limitations; nevertheless, to the best of our knowledge, few works have applied non-isothermal kinetics based on the isoconversional and model approach principles for studying such valuable alternative sources of energy such as peat. We hope that the present work could be used to generate the interest of other researchers into developing investigations into peat in further research.

5. Conclusions

This work describes the behavior of the peat oxidation process in addition to its kinetic aspect by means of thermogravimetric and differential scanning calorimetric analysis. The evidence from this study points toward the idea that the peat oxidation process has oil-like oxidation behavior. In general, these results suggest that the peat oxidation process includes two main oxidation regions: LTO and HTO processes. Our research underlined the importance of using iron tallate as an effective catalyst for the peat oxidation process. The comprehensive results demonstrated that iron tallate decreases the energy in the activation of the LTO and HTO of peat. Moreover, the findings of this study support the idea that iron tallate effectively increases the peat oxidation process rate in both the LTO and HTO regions which results in increased light hydrocarbon generation during the LTO region on larger scales. These findings add to the growing body of the literature on peat development and exploitation as alternative sources of energy for future generations. Our work has limitations. Despite this, we believe our work could be a springboard for further analysis and studies about the kinetic behavior of peat in the presence of catalysts in addition to the investigation of their mechanism during their application. In our view, these findings present an excellent initial step towards developing and exploiting peat for generating energy in different industrial plants by means of in situ combustion, which is widely considered an economically effective method for generating hydrocarbons and energy. We are currently in the process of investigating the effect of different catalysts with different characteristics on the kinetic behavior of peat oxidation and pyrolysis processes. However, it is recommended that further research should be undertaken in thermodynamics and the mass and energy transfer associated with peat oxidation to validate our findings by utilizing a larger sample size. Another important aspect that should be taken into consideration is the electrochemical analysis of the processes of peat oxidation which is possible due to the generation of electrons through oxidation.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11111344/s1>, Table S1: Kinetic parameters of peat oxidation process in the presence and absence of iron tallate obtained by the model approach of non-isothermal kinetics during experiments.

Author Contributions: Formal analysis, investigation, writing—original draft, visualization, M.A.K.; formal analysis, data curation, visualization, S.E.L.; formal analysis, investigation, N.E.I.; formal analysis, investigation, A.A.E.; formal analysis, investigation, M.Y.G.; investigation, visualization, N.Y.P.; formal analysis, investigation, visualization, T.O.K.; formal analysis, investigation, visualization, funding acquisition, A.V.V. All authors discussed and approved the final version. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: This work was supported by the Ministry of Science and Higher Education of the Russian Federation under agreement No. 075-15-2020-931 within the framework of the development program for a world-class Research Center “Efficient development of the global liquid hydrocarbon reserves”.

Conflicts of Interest: The authors declare that there is no conflict of interest regarding the publication of this paper.

References

- Wang, L.; Kong, F.; Zheng, M.; Wang, D. Present Situation and Suggestions on the Exploitation and Utilization of Peat Resources in China. *Conserv. Util. Miner. Resour.* **2019**, *39*, 142–147.
- Waller, M.; Kirby, J. Coastal peat-beds and peatlands of the southern North Sea: Their past, present and future. *Biol. Rev.* **2021**, *96*, 408–432. [[CrossRef](#)]
- Lee, T.; Jung, S.; Hong, J.; Wang, C.-H.; Alessi, D.S.; Lee, S.S.; Park, Y.-K.; Kwon, E.E. Using CO₂ as an oxidant in the catalytic pyrolysis of peat moss from the north polar region. *Environ. Sci. Technol.* **2020**, *54*, 6329–6343. [[CrossRef](#)] [[PubMed](#)]
- Gu, J.; Wang, S.; Lu, T.; Wu, Y.; Yuan, H.; Chen, Y. Synthesis and evaluation of pyrolysis waste peat char supported catalyst for steam reforming of toluene. *Renew. Energy* **2020**, *160*, 964–973. [[CrossRef](#)]
- Fuchsman, C. *Peat: Industrial Chemistry and Technology*; Elsevier: Amsterdam, The Netherlands, 2012; ISBN 0323157114.
- Elliott, D.C.; Baker, E.G.; Piskorz, J.; Scott, D.S.; Solantausta, Y. Production of liquid hydrocarbon fuels from peat. *Energy Fuels* **1988**, *2*, 234–235. [[CrossRef](#)]
- Weldemichael, Y.; Assefa, G. Assessing the energy production and GHG (greenhouse gas) emissions mitigation potential of biomass resources for Alberta. *J. Clean. Prod.* **2016**, *112*, 4257–4264. [[CrossRef](#)]
- Shuba, E.S.; Kifle, D. Microalgae to biofuels: ‘Promising’ alternative and renewable energy, review. *Renew. Sustain. Energy Rev.* **2018**, *81*, 743–755. [[CrossRef](#)]
- Marsh, G. Biofuels: Aviation alternative? *Renew. Energy Focus* **2008**, *9*, 48–51. [[CrossRef](#)]
- Yang, Q.Z.; Song, B. Sustainability assessment of biofuels as alternative energy resources. In Proceedings of the 2008 IEEE International Conference on Sustainable Energy Technologies, Singapore, 24–27 November 2008; pp. 1001–1006.
- Sternik, D.; Wiśniewska, M.; Nowicki, P. Thermal degradation of peat-based activated carbons covered with mixed adsorption layers of PAA polymer and SDS surfactant. *Thermochim. Acta* **2019**, *676*, 71–83. [[CrossRef](#)]
- Klein, K.; Gross-Schmölders, M.; De la Rosa, J.M.; Alewell, C.; Leifeld, J. Investigating the influence of instrumental parameters and chemical composition on pyrolysis efficiency of peat. *Commun. Soil Sci. Plant Anal.* **2020**, *51*, 1572–1581. [[CrossRef](#)]
- Taherzadeh, M.J.; Karimi, K. Acid-based hydrolysis processes for ethanol from lignocellulosic materials: A review. *BioResources* **2007**, *2*, 472–499.
- Taherzadeh, M.J.; Karimi, K. Enzymatic-based hydrolysis processes for ethanol from lignocellulosic materials: A review. *BioResources* **2007**, *2*, 707–738.
- Wen, Y. *Study of the Performance of Peat Moss Pyrolysis*; Kth Royal Institute of Technology: Stockholm, Sweden, 2019.
- Maftu’ah, E.; Fahmi, A.; Hayati, A. Changes in degraded peat land characteristic using FTIR-spectroscopy. In Proceedings of the IOP Conference Series: Earth and Environmental Science; IOP Publishing: Bandung, Indonesia, 2019; Volume 393, p. 12091.
- Kirkinen, J.; Minkinen, K.; Penttilä, T.; Kojola, S.; Sievänen, R.; Alm, J.; Saarnio, S.; Silvan, N.; Laine, J.; Savolainen, I. *Greenhouse Impact due to Different Peat Fuel Utilisation Chains in Finland—A Life-Cycle Approach*; Boreal Environment Research Publishing Board: Helsinki, Finland, 2007.
- Lake, L.W. *Enhanced Oil Recovery*; Prentice Hall: Englewood Cliffs, NJ, USA, 1989.
- Sitnov, S.; Mukhamatdinov, I.; Aliev, F.; Khelkhal, M.A.; Slavkina, O.; Bugaev, K. Heavy oil aquathermolysis in the presence of rock-forming minerals and iron oxide (II, III) nanoparticles. *Pet. Sci. Technol.* **2020**, *38*, 574–579. [[CrossRef](#)]
- Sheng, J.J. *Modern Chemical Enhanced Oil Recovery: Theory and Practice*; Gulf Professional Publishing: Houston, TX, USA, 2010; ISBN 0080961630.
- Vakhin, A.V.; Khelkhal, M.A.; Tajik, A.; Gafurov, M.R.; Morozov, O.G.; Nasybullin, A.R.; Karandashov, S.A.; Ponomarev, A.A.; Krapivnitskaia, T.O.; Glyavin, M.Y. The Role of Nanodispersed Catalysts in Microwave Application during the Development of Unconventional Hydrocarbon Reserves: A Review of Potential Applications. *Processes* **2021**, *9*, 420. [[CrossRef](#)]
- Green, D.W.; Willhite, G.P. *Enhanced oil Recovery*; Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers: Richardson, TX, USA, 1998; Volume 6.
- Mukhamatdinov, I.I.; Salih, I.S.S.; Khelkhal, M.A.; Vakhin, A.V. Application of Aromatic and Industrial Solvents for Enhancing Heavy Oil Recovery from the Ashalcha Field. *Energy Fuels* **2020**, *35*, 374–385. [[CrossRef](#)]
- Mokheimer, E.M.A.; Hamdy, M.; Abubakar, Z.; Shakeel, M.R.; Habib, M.A.; Mahmoud, M. A comprehensive review of thermal enhanced oil recovery: Techniques evaluation. *J. Energy Resour. Technol.* **2019**, *141*, 30801. [[CrossRef](#)]
- Mahinpey, N.; Ambalae, A.; Asghari, K. In situ combustion in enhanced oil recovery (EOR): A review. *Chem. Eng. Commun.* **2007**, *194*, 995–1021. [[CrossRef](#)]
- Farhadian, A.; Khelkhal, M.A.; Tajik, A.; Lapuk, S.E.; Rezaeisadat, M.; Eskin, A.A.; Rodionov, N.O.; Vakhin, A.V. Effect of Ligand Structure on the Kinetics of Heavy Oil Oxidation: Toward Biobased Oil-Soluble Catalytic Systems for Enhanced Oil Recovery. *Ind. Eng. Chem. Res.* **2021**, *60*, 14713–14727. [[CrossRef](#)]
- Burger, J.G.; Sahuquet, B.C. Chemical Aspects of in-Situ Combustion—Heat of Combustion and Kinetics. *Soc. Pet. Eng. J.* **1972**, *12*, 410–422. [[CrossRef](#)]
- Sarathi, P. *In-Situ Combustion Handbook—Principles and Practices*; National Petroleum Technology Office: Tulsa, OK, USA, 1999.
- Lin, C.Y.; Chen, W.H.; Lee, S.T.; Culham, W.E. Numerical simulation of combustion tube experiments and the associated kinetics of in-situ combustion processes. *Soc. Pet. Eng. J.* **1984**, *24*, 657–666. [[CrossRef](#)]
- Abuhesa, M.B.; Hughes, R. Comparison of conventional and catalytic in situ combustion processes for oil recovery. *Energy Fuels* **2009**, *23*, 186–192. [[CrossRef](#)]

31. Moore, R.G.; Laureshen, C.J.; Mehta, S.A.; Ursenbach, M.G.; Belgrave, J.D.M.; Weissman, J.G.; Kessler, R.V. A downhole catalytic upgrading process for heavy oil using in situ combustion. *J. Can. Pet. Technol.* **1999**, *38*. [[CrossRef](#)]
32. Papavasiliou, J.; Avgouropoulos, G.; Ioannides, T. In situ combustion synthesis of structured Cu-Ce-O and Cu-Mn-O catalysts for the production and purification of hydrogen. *Appl. Catal. B Environ.* **2006**, *66*, 168–174. [[CrossRef](#)]
33. Khelkhal, M.A.; Eskin, A.A.; Nurgaliev, D.K.; Vakhin, A.V. Thermal Study on Stabilizing the Combustion Front via Bimetallic Mn@Cu Tallates during Heavy Oil Oxidation. *Energy Fuels* **2020**, *34*, 5121–5127. [[CrossRef](#)]
34. Khelkhal, M.A.; Eskin, A.A.; Vakhin, A.V. Kinetic Study on Heavy Oil Oxidation by Copper Tallates. *Energy Fuels* **2019**, *33*, 12690–12695. [[CrossRef](#)]
35. Galukhin, A.; Nosov, R.; Eskin, A.; Khelkhal, M.; Osin, Y. Manganese Oxide Nanoparticles Immobilized on Silica Nanospheres as a Highly Efficient Catalyst for Heavy Oil Oxidation. *Ind. Eng. Chem. Res.* **2019**, *58*, 8990–8995. [[CrossRef](#)]
36. Feoktistov, D.A.; Kayukova, G.P.; Vakhin, A.V.; Sitnov, S.A. Catalytic Aquathermolysis of High-Viscosity Oil Using Iron, Cobalt, and Copper Tallates. *Chem. Technol. Fuels Oils* **2018**, *53*, 905–912. [[CrossRef](#)]
37. Fassihi, M.R.; Brigham, W.E.; Ramey, H.J. Reaction Kinetics of in-Situ Combustion: Part 1—Observations. *Soc. Pet. Eng. J.* **1984**, *24*, 399–407. [[CrossRef](#)]
38. Bousaid, I.S.; Ramey, H.J. Oxidation of Crude Oil in Porous Media. *Soc. Pet. Eng. J.* **1968**, *8*, 137–148. [[CrossRef](#)]
39. Vyazovkin, S.; Burnham, A.K.; Criado, J.M.; Pérez-Maqueda, L.A.; Popescu, C.; Sbirrazzuoli, N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim. Acta* **2011**, *520*, 1–19. [[CrossRef](#)]
40. Lapuk, S.E.; Zubaidullina, L.S.; Ziganshin, M.A.; Mukhametzyanov, T.A.; Schick, C.; Gerasimov, A.V. Kinetic stability of amorphous solid dispersions with high content of the drug: A fast scanning calorimetry investigation. *Int. J. Pharm.* **2019**, *562*, 113–123. [[CrossRef](#)] [[PubMed](#)]
41. Kissinger, H.E. Variation of peak temperature with heating rate in differential thermal analysis. *J. Res. Natl. Bur. Stand. (1934)* **1956**, *57*, 217. [[CrossRef](#)]
42. Kissinger, H.E. Reaction Kinetics in Differential Thermal Analysis. *Anal. Chem.* **1957**, *29*, 1702–1706. [[CrossRef](#)]
43. Friedman, H.L. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. *J. Polym. Sci. Part C Polym. Symp.* **1964**, *6*, 183–195. [[CrossRef](#)]
44. Lapuk, S.E.; Mukhametzyanov, T.A.; Schick, C.; Gerasimov, A.V. Crystallization kinetics and glass-forming ability of rapidly crystallizing drugs studied by Fast Scanning Calorimetry. *Int. J. Pharm.* **2021**, *599*, 120427. [[CrossRef](#)] [[PubMed](#)]
45. Lapuk, S.E.; Mukhametzyanov, T.A.; Schick, C.; Gerasimov, A.V. Kinetic stability of amorphous dipyrindamole: A fast scanning calorimetry investigation. *Int. J. Pharm.* **2020**, *574*, 118890. [[CrossRef](#)]
46. Freund, J.E.; Perles, B.M. *Modern Elementary Statistics*; Pearson College Division: Upper Saddle River, NJ, USA, 2007.