ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

COMBUSTION KINETICS OF ASPHALTITES COMPARED TO COALS THROUGH ISOCONVERSIONAL ANALYSIS

M.Sc. THESIS

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Department of Petroleum and Natural Gas Engineering

Petroleum and Natural Gas Engineering Programme

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

ASFALTİTLERİN YANMA KİNETİĞİNİN EŞDÖNÜŞÜM YÖNTEMİYLE KÖMÜRLERLE KARŞILAŞTIRILMASI

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To my family,

FOREWORD

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ABBREVIATIONS

ABD : Amerika Birleşik Devletleri
ASTM : American Society for Testing and Materials
CMG : Computer Modeling Group
DAQ : Data Acquisition
DSO : Düşük Sıcaklık Oksidasyonu
HTO : High-Temperature Oxidation
ITU : Istanbul Technical University
LHS : Left Hand Side
LTO : Low Temperature Oxidation
MATLAB : Matrix Laboratory
MCC : Measurement Computing Corporation
OOIP : Original Oil In Place
RHS : Right Hand Side
SE : Southeastern
TSR : Thermochemical Sulfate Reduction
USA : United States of America
USB-TC : Universial Serial Bus-Temprature Control
YSO : Yüksek Sıcaklık Oksidasyonu

SYMBOLS

μ	: Micrometer
r	: Reaction Rate
K	: Reaction Rate Constant
T	: Temprature
C	: Concentration
A	: Pre-exponential Factor
E	: Activation Energy
R	: Gas Constant
x	: Conversion
t	: Time

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COMBUSTION KINETICS OF ASPHALTITES COMPARED TO COALS THROUGH ISOCONVERSIONAL ANALYSIS

SUMMARY

Asphaltites are dark-colored solid petroleum, classified as a group of Bitumens based on the latest classifications; this is disputable. They are formed by alteration during or after migration, generally in oil-bearing zones. They are primarily observed in petroleum provinces. In Turkey, they are extensively observed in the southeastern and some northern parts and are commonly produced by surface mining techniques for electricity generation. On the other hand, gilsonite, a form of asphaltite produced in the US (Uinta Basin of Northeastern Utah), is used as an additive for different purposes.

Asphaltites originated from conventional oil. However, they have coal-like properties, such as ash content. It would be worthwhile if kinetic signatures could be compared to coal and petroleum. In this way, a more persistent picture of asphaltite combustion characteristics is clarified. Understanding this helps to decide on information about the reaction scheme, activation energy, and general combustion behavior, and finally, the reactions probably taking place in this procedure of newly trend alternative source of energy. For this purpose, a similar set of experiments is carried out with coal, and using literature, it is compared to petroleum, respectively.

This experimental work analyzes the combustion characteristics of asphaltite from the Şırnak province of Turkey through kinetic-cell experiments. Five sets of ramped temperature experiments are conducted using a 2 g asphaltite sample with different heating rates. These experiments measure the temperature inside the cell and the effluent gas composition, primarily CO, CO2, CH4, and O2 concentrations. The results indicate two O2 consumption peaks at different temperatures, corresponding to High-Temperature Oxidation (HTO) and Low-Temperature Oxidation (LTO). Before doing any analysis, some comments compared to coal and asphaltite raw data, such as the initial temperature of LTO and HTO reactions, oxygen consumption, and carbon dioxide production rates. Then, the results are analyzed using isoconversional methods. These methods require a set of experiments conducted at different heating rates and result in a so-called isoconversional fingerprint (Conversion versus activation energy).

The objective of the kinetic analysis is obtaining the activation energy without assuming any kinetic model under the isoconversional assumption that the reaction rate at a constant extent of conversion is only a function of temperature. This fingerprint provides information on the reaction scheme. The same analysis was repeated using carbon monoxide and carbon dioxide production data. Carbon monoxide data does not show reliable and sufficiently accurate results. However, taking carbon dioxide data into analysis contributes significantly to figuring out the reaction scheme that might have taken place in the gasification process.

Considering that asphaltites are mostly treated as coals in some regions and literature, and the procedures and processes applied to them are almost the same, it is expected

to show further similarities with coals. Yet, regarding classifications, crude oil shows a closer relationship to asphaltites. Asphaltites have been proven to exhibit complex behavior regarding activation energy trends, making it hard to comment on their characteristics or reaction schemes. Therefore, a commercial simulator is used to model the gasification experiments based on coal reactions to get a better understanding. Using this commercial simulator determines the behavior of coal in the gasification process and provides a better understanding of the governing reaction. Reservoir and sample characteristics and properties, geology, reactions, heating systems, imposed heating rates, and kinetic parameters are entered as input data into the simulator.

The simulation showed that carbon oxidation plays the most crucial role in the gasification process in terms of both activation energy determination and consumption rates. Furthermore, these reactions occur in the most critical phase of the gasification procedure, namely, low and high-temperature oxidations in the intermediate gasification steps. Moreover, almost all the main gasification reactions occur in the last gasification phases. Therefore, it can be concluded that the extent of the gasification of coal and asphaltite tends to behave the same in the previous phases, and the mechanisms and reactions in the final steps of asphaltite gasification are similar to coal.

ASFALTİTLERİN YANMA KİNETİĞİNİN EŞDÖNÜŞÜM YÖNTEMİYLE KÖMÜRLERLE KARŞILAŞTIRILMASI

ÖZET

Asfaltitler, organik madde içeriği yüksek olan ve genellikle petrol içeren bölgelerde bulunan koyu renkli katı petrol ürünleridir. Bu maddeler, genellikle kükürt, azot ve metal içerikleri yönünden zengindir. Asfaltitlerin oluşumu genellikle göç sırasında veya sonrasında gerçekleşir. Petrolün oluşumu sırasında organik maddelerin yüksek basınç ve sıcaklık altında dönüşümüyle meydana gelirler.

Asfaltitler, genellikle yüzey madenciliği teknikleriyle çıkarılır. Bu teknikler arasında açık ocak madenciliği ve kırma-eleme işlemleri bulunur. Ayrıca, asfaltitlerin çıkarılması için yer altı madenciliği de kullanılabilir. Asfaltitler, çıkarıldıktan sonra farklı endüstriyel uygulamalar için kullanılır.

Asfaltitlerin birçok endüstriyel kullanım alanı vardır. Özellikle elektrik üretimi için kullanılan termal santrallerde yakıt olarak kullanılırlar. Ayrıca, asfaltitler yol yapımında da yaygın olarak kullanılır. Yol asfaltı üretiminde, asfaltitlerin karışımına katılarak dayanıklı ve uzun ömürlü yolların yapımına katkı sağlarlar.

Türkiye'de, güneydoğu ve bazı kuzey bölgelerde bulunan asfaltit yatakları, genellikle yüzey madenciliği teknikleri kullanılarak çıkarılırBu bölgelerdeki asfaltit yatakları, genellikle elektrik üretimi için kullanılır.

ABD'de ise Uinta Havzası'nda üretilen gilsonit adı verilen bir asfaltit çeşidi bulunmaktadır. Gilsonit, farklı endüstriyel amaçlar için kullanılan bir asfaltit türüdür. Özellikle yapıştırıcı, sızdırmazlık malzemesi, boya ve vernik üretimi gibi farklı endüstrilerde kullanılır.

Asfaltitlerin çıkarılması ve kullanımı, farklı coğrafi bölgelere göre değişiklik gösterebilir. Türkiye'de elektrik üretimi için kullanılan asfaltitlerin yanı sıra, ABD'de farklı endüstriyel amaçlar için kullanılan gilsonit gibi özel asfaltit türleri de bulunmaktadır. Bu durum, asfaltitlerin farklı kullanım alanlarına ve endüstrilere yönelik özel özelliklere sahip olabileceğini göstermektedir.

Asfaltitlerin kömür benzeri özelliklere sahip olduğu bilinmektedir. Bu nedenle, asfaltitin yanma özellikleri kömür ve petrolle karşılaştırılarak daha kesin bir şekilde açıklanabilir. Bu anlayış, asfaltitin reaksiyon şeması, aktivasyon enerjisi şeması ve genel davranışı hakkında bilgi sağlayarak, alternatif enerji kaynağı olarak kullanım potansiyelini ortaya koymaktadır. Bu konuda yapılan araştırmalar genellikle asfaltitlerin kömür ve petrole benzerliklerini incelemekte ve bu maddelerin enerji üretimi için potansiyelini ortaya koymayı amaçlamaktadır. Bu çalışmalar, asfaltitlerin enerji üretimi için alternatif bir kaynak olabileceğini göstermektedir.

Asfaltitlerin yanma özelliklerini daha kesin bir şekilde açıklamak, bu alternatif enerji kaynağının potansiyelini anlamak ve kullanımını optimize etmek için önemli bir adımdır.

Asfaltitlerin yanma özellikleri incelendiğinde, reaksiyon hızı, yanma sıcaklığı, yanma verimliliği ve oluşan emisyonlar gibi faktörlerin belirlenmesi gerekmektedir. Bu veriler, asfaltitlerin enerji üretimi potansiyelini değerlendirmek ve yanma sürecinde meydana gelen kimyasal reaksiyonları anlamak için kritik öneme sahiptir. Yanma sırasında oluşan emisyonların bileşimi ve miktarı, asfaltitlerin çevresel etkilerini anlamak ve kontrol etmek için önemlidir. Bu bilgiler, asfaltitlerin enerji endüstrisindeki rolünü ve sürdürülebilirliğini değerlendirmek için kullanılabilir.

Bu amaçla, kömür gazlaştırılmasına benzer bir dizi deney gerçekleştirilmiş ve literatürdeki çalışmalar değerlendirilerek petrolle karşılaştırılmıştır. Bu şekilde, asfaltit yanma karakteristiklerinin daha net bir resmi ortaya çıkar. Bu da reaksiyon şeması, aktivasyon enerjisi şeması ve genel davranış hakkında bilgi vermede yardımcı olur. Bu nedenle, bu prosedürde muhtemelen gerçekleşen reaksiyonlar hakkında bilgi vermede yardımcı olur. Bu amaçla, kömürle benzer bir dizi deney yapılarak literatür kullanılarak sırasıyla petrolle karşılaştırılır.

Bu deneysel çalışmada, Türkiye'nin Şırnak ilinden elde edilen asfaltitin yanma özellikleri kinetik hücre deneyleri yoluyla analiz edilmiştir. 2 gram asfaltit numunesi kullanılarak farklı ısıtma hızlarıyla beş deney seti yapılmıştır. Bu deneylerde, hücre içindeki sıcaklık ve gaz bileşimi ölçülmüş; başlıca CO, CO2, CH4 ve O2 konsantrasyonları belirlenmiştir. Sonuçlar, farklı sıcaklıklarda iki farklı O2 tüketim zirvesini göstermekte olup, bu zirveler Yüksek Sıcaklık Oksidasyonu (HTO) ve Düşük Sıcaklık Oksidasyonu (LTO) ile ilişkilidir.

Herhangi bir analiz yapmadan önce, asfaltit ve kömür ham verileri karşılaştırılarak LTO ve HTO reaksiyonlarının başlangıç sıcaklıkları, oksijen tüketimi ve karbondioksit üretim oranları gibi bazı yorumlar yapılmıştır. Daha sonra, sonuçlar eş-dönüşüm yöntemi kullanılarak analiz edilmiştir. Bu yöntemler, farklı ısıtma hızlarında yapılan deney setlerini gerektirir ve bu deneyler sonucunda "dönüşüm-aktivasyon enerjisi" olarak adlandırılan bir eş-dönüşüm parmak izi elde edilir. Kinetik analizin amacı, sıcaklık fonksiyonu olarak kabul edilen sabit bir dönüşüm derecesindeki reaksiyon hızının herhangi bir kinetik model varsayımı yapmadan aktivasyon enerjisini elde etmektir. Bu parmak, izi reaksiyon şeması hakkında bilgi sağlar. Karbon monoksit ve karbondioksit üretim oranları için de aynı analiz yapılmıştır. Karbon monoksit verileri güvenilir ve yeterince doğru sonuçlar göstermemektedir. Bununla birlikte, karbondioksit verilerinin analiz edilmesi, gazlaştırma sürecinde gerçekleşmiş olabilecek reaksiyon şemasını anlamaya büyük katkı sağlamaktadır.

Asfaltitlerin bazı bölgelerde ve literatürde genellikle kömürler gibi işlendiğini ve uygulanan prosedürlerin ve süreçlerin neredeyse aynı olduğunu göz önünde bulundurarak, sınıflandırmalar söz konusu olduğunda ham petrolün asfaltitlere daha yakın bir ilişki gösterdiği beklenmektedir. Asfaltitlerin aktivasyon enerjisi eğilimleri açısından karmaşık bir davranış sergilediği ve bu nedenle özellikleri veya reaksiyon şeması hakkında yorum yapmanın zor olduğu anlaşılmaktadır. Bu nedenle, daha iyi bir anlayış elde etmek için kömür gazlaştırma deneylerini modellemek için ticari bir simülatör kullanılmıştır. Bu ticari simülasyon aracılığıyla kömürün gazlaştırma sürecindeki davranışı belirlenmiş ve ayrıca etkin reaksiyonun anlaşılmasına öenmli katkı sağlayacaktır. Rezervuar ve numune özellikleri, jeoloji, reaksiyonlar, ısıtma sistemleri, uygulanan ısıtma hızları ve kinetik parametreler girdi verileri olarak simülatöre girilmiştir. Simülasyondan elde edilen sonuçlara göre, karbon oksidasyonunun hem aktivasyon enerjisi belirleme hem de tüketim oranları açısından gazlaştırma sürecinde en önemli rolü oynadığı anlaşılmıştır. Ayrıca, bu reaksiyon gazlaştırmanın en önemli aşaması olan; gazlaştırmanın ara aşamalarında gerçekleşen

düşük ve yüksek sıcaklık oksidasyonlarında gerçekleşmektedir. Dahası, neredeyse tüm ana gazlaştırma reaksiyonlarının gazlaştırmanın son aşamalarında gerçekleştiği görülmektedir; bu nedenle, açıkça kömür ve asfaltitin son aşamalarda benzer davranma eğiliminde olduğu göz önünde bulundurulduğunda, asfaltit gazlaştırmanın son adımlarında gerçekleşen mekanizma ve reaksiyonların kömürle benzer olduğu sonucuna varılabilir.

1. INTRODUCTION

With the rising demand for energy consumption day by day, it is vital to consider alternative energy resources to guarantee the current needs and sustain the world of energy for the future. Even though renewable energies have come into play in recent years, they seem like they need to be more abundant to supply the current demand. Thus, conventional resources are still preferable since they are affordable and well-known. For instance, coal still sustains the second rank up to this time, while asphaltite is almost a new and unexplored energy source (Rapier, 2023). Furthermore, the statistics also show that consumption of these resources is placed in the primary ranks despite decreasing in recent years (Rapier, 2023). Among all the convenient traditional resources, reinvented ways of better utilization of coals, such as gasification, seem attractive in the last few years since they can potentially be the intermediary between traditional and renewable energy sources using new technological advancements. Asphaltites are among those fossil fuels that are potential gasification candidates.

On the other hand, environmental concerns have been debated in recent decades. Coals generally contain more carbon content than crude oil; thus, they emit more greenhouse gases during combustion and in power plants (Rapier, 2003). Typically, asphaltites are sulfur-rich and contain heavy contents like tars that emit several hazardous pollutions during combustion besides carbon dioxide emissions. Furthermore, numerous issues are attributed to them in mining, such as water pollution. Considering the environmental issues related to traditional resources, such as various pollutions, emissions, and mining exploitation methods, the need to apply innovative techniques and use modern technologies to exploit them emerges.

Over the recent years, much literature has discussed the gasification process of these two resources as a possible alternative. As the world seeks to transition towards low-carbon consumption, there is a growing need for innovative technologies that can provide clean and reliable energy sources. Gasification offers a pathway to utilize

various sources of so-called 'non-renewable' energy for clean energy production. It guarantees to address a wide range of environmental, pollution, and disposal challenges by producing relatively cleaner energy and chemicals called synthesis gases. Improved gasification technologies have led to increased efficiency, higher syngas quality, and more technical compliance. These advancements have expanded the range of potential applications for gasification across various sectors, including power generation, industrial processes, and cleaner product advantages. Therefore, the gasification of asphaltite and coal resources, considering both technological advancements and sustainability approaches, makes it an alternative extraction method.

1.1 Asphaltites

Despite their widespread applications in different industries, asphaltites have yet to be discussed sufficiently in the literature. These days, with technological advancement, they are an intriguing subject of study. Since ancient civilizations, asphaltites have been used worldwide for different purposes in diverse forms in daily life, including construction in different fields, waterproofing, weapons, and as a fuel in Greece, India, Egypt, etc. (Krishnan and Rajagopal, 2003). It is worth mentioning that asphaltite, or generally so-called bituminous materials according to The American Society for Testing and Materials (ASTM), have been used with various names in different resources of history, primarily based on their origins (ASTM, 2000). This suggests that asphaltites were always on hand in the early times. However, after the Industrial Revolution, it gained attraction to a greater extent on account of its crucial role in different sectors of the construction industry and fuel applications, which led to an increase in the exploration of asphaltite resources in different regions (Krishnan and Rajagopal, 2003).

Asphaltites are dark solid petroleum-derived matter that is classified as the bitumen group. Asphaltites have high melting points and are soluble in carbon disulfide (Hunt, 1979). They are also subdivided into three categories: grahamite, gilsonite, and glance pitch (Hunt, 1979). Different properties can characterize these subdivisions; however, the most commonly used factor is the carbon number (Kelso and Powell, 1944). They are usually abundant in petroleum-bearing zones like sedimentary rocks (Hosseini, 2018). Asphaltite deposits are observed frequently in America, Australia, Sweden,

Turkey, Argentina, Russia, and Iran (Gordadze et al., 2018). Asphaltites are generally formed through alteration processes called metamorphism in oil-bearing zones during hydrocarbon migration (Hamamci et al., 1997). In other words, due to tectonic movements, it becomes heavier during crude oil's migration due to the loss of the lighter components (Snape, 1995). Subsequently, due to imposing numerous chemical and physical mechanisms, such as biodegrading and oxidation, based on geological and alteration conditions, the H/C ratio decreases, and asphaltites are formed (Snape, 1995). Asphaltites consist of complex heavy compounds, namely non-polar aliphatic and naphthenic hydrocarbons to highly polar aromatic molecules that consist of heteroatoms such as oxygen, nitrogen, and sulfur as studied by Sert et al. (2008) and some elements like vanadium and nickel and some radioactive metals such as uranium and thorium (Aksogan Korkmaz and Ozbas, 2017). Asphaltites generally have high caloric value and softening points ranging from 200-315 °C. Asphaltite extraction involves surface mining techniques and is usually determined by several factors, such as asphaltite characteristics (Hosseini, 2018). Also, considering their environmental hazards and emissions, in situ extractions and underground gasification can be applied, the second of which is investigated in this study in kinetic scale laboratory experiments.

1.1.1 Asphaltite in Turkey

In Turkey, asphaltite studies are of more importance since there is a remarkable occurrence of asphaltite deposits of approximately 77.5 million tonnes, as stated by Sert et al. (2008), especially in southeastern and northern regions. In the southeast part of Turkey, where considerable reserves of asphaltite lay, the deposits are pervaded in Siirt, Şırnak, Hakkari, and Silopi (Aksogan Korkmaz and Ozbas, 2017; Hamamci et al., 1997). Nevertheless, in the northern part, it is observed in Amasya (Kara-Gulbay and Korkmaz, 2013). Turkey's quality of asphaltite resources is poor compared to other sites since the ash and sulfur content is usually higher (Hamamci et al., 1997). Therefore, specific performance tests and technologies are needed to ensure its clean production and also to investigate its eligibility (Tosun, 2013). As mentioned, carbon numbers are the most common way of categorizing asphaltites (Kelso and Powell, 1944). In this way, as long as Turkey's asphaltites are considered, gilsonites have the least fixed carbon of nearly 10%, and grahamite has the most fixed carbon content of approximately 55% (Kelso and Powell, 1944). In Turkey, asphaltites show

characteristics between asphaltite and pyrobitumens, and they are sometimes associated with mineral matters generally called Grahamites (Kelso and Powell, 1944; Tonbul et al., 2006). Historically, asphaltite applications in Turkey have become more prevalent after the 1970s, as stated by Hamamci et al. (1997), for heating, production of ammonia, as a source of trace materials, and conversion into refinery by-products like light hydrocarbon gases, tar, and high-quality fuel char (Altun et al., 2003; Elbeyli, 2006; Hamamci et al., 1997).

1.2 Asphaltite Gasification

Asphaltite gasification has been a stimulating study topic in some regions like Argentina and Turkey (Fouga et al., 2011; Tosun, 2013). Since the last decade, it has been mentioned more as it provides using one alternative relatively unclean source of energy in different fields by means of producing other valuable, environmentally friendly products, namely syngas (Fouga et al., 2011). This way, co-electricity production projects, methane production optimization, and carbon dioxide capture can be performed by managing a gasification plant (Tosun, 2013). For these projects to be practical and optimized, in the first instance, experiments should be conducted to predict, confirm, and calibrate the process (Shurtz and Fletcher, 2009). By doing this, different parameters, such as kinetic parameters, heating rate impacts, and probable reactions and mechanisms, are considered and analyzed (Shurtz and Fletcher, 2009).
Gasification itself is a partial combustion process; in a sense, abundance or lack of oxygen controls the process. During the gasification process, a gasifying agent, such as oxygen, is injected into the reactor, and meanwhile, the reactor is heated with the desired heating rate; syngas are produced and measured simultaneously. In fact, the gasification process initiates with pyrolysis reactions and proceeds with gasification reactions. However, determining a series of reactions and kinetic parameters such as activation energy is a complex process for asphaltites since they seem to show various behaviors depending on the type and properties (Fouga et al., 2011; Tosun, 2013). This comes from the point that they have the physical appearance of coal, but they are derived from crude oil as studied (Aksogan Korkmaz and Ozbas, 2017), and there still needs to be a general agreement on their definition (Tosun, 2013). Hence, comparing asphaltite gasification behavior with both would contribute to a better understanding of it. Furthermore, it is valuable to simulate the gasification process since, in this way,

an approximate idea about the reaction mechanisms and stages in different applicable conditions are considered (Labojko et al., 2012). This will be a significant help not only in the optimization of the coal gasification process but also in realizing the asphaltites.

As mentioned before, obtaining valid data is the most crucial fundamental step (Labojko et al., 2012). Following that, analysis methods also play an essential role since an accurate analysis is necessary to define the mechanisms taking place and evaluate the kinetic parameters (Labojko et al., 2012). Therefore, considering the complexity of the samples in this study, the isoconversional method is used for kinetic analysis. This approach is based on the Arrhenius equation and independent of the reaction model (Mei and Guo, 2022). The isoconversional principle states that the reaction rate at a constant conversion is only dependent on the temperature (Mei and Guo, 2022).

1.3 Statement of Problem

Asphaltite resources in Turkey are primarily used as a coal substitute in power plants for electricity generation. However, their high sulfur content poses environmental challenges. Additionally, many of these resources are unsuitable for underground mining. Consequently, asphaltites in Turkey show great potential for gasification. Gasification is a partial combustion process applicable to coals of various ranks, yet there is no documented underground gasification of asphaltites. To address this, initial kinetic-scale experiments are necessary to understand the behavior of asphaltites during gasification better. Through these experiments, the kinetic parameters and probable reaction mechanisms can be analyzed, along with conditions such as temperature and pressure, ultimately leading to more efficient industrial-scale gasification processes. Since gasification is a process used for coals, it is essential to compare the combustion kinetics of coal and asphaltites through kinetic experiments to gain a comprehensive understanding of asphaltite gasification.

1.4 Thesis Overview

In this study, gasification is carried out on a kinetic scale on Şırnak asphaltite at different heating rates. The same set of experiments was conducted on Soma coals for

comparison. The system setup, kinetic analysis, methods and materials, and conclusions are discussed in later chapters. Eventually, a gasification model is simulated for coal to get an idea of reaction schemas and optimize kinetic parameters, mainly activation energy.

2. LITERATURE REVIEW

2.1 Introduction

In recent decades, asphaltites have been the primary subject of debate in literature not only due to their several applications in a variety of industries but also because they seem to be an attractive alternative utilization technique for fossil fuels. Since they are abundant in petroleum provinces, as mentioned in Curiale (1986), investigating them has become an interesting research topic for petroleum and mining engineers. Reviewing the literature gives this idea that there is no agreement on their true nature, as stated by Tosun (2013), because the same controversy is valid for its origin (Hosseini, 2018).

In order to understand the nature of asphaltites and, subsequently, their implementations, it is essential to deeply understand their origin, formation, compositions, and classifications. Asphaltite and its relative materials are believed to be a subdivision of the group of heavy hydrocarbons called solid bitumens. Thus, here, at the first instance, the term Bitumen and all the necessary information regarding it must be discussed and defined correctly, followed by asphaltites, which are determined based on the presumed knowledge obtained. Eventually, one of the latest research fields on asphaltites, the gasification of asphaltites, will be explored in a few words.

2.2 Bitumens

Bitumens are the origin of the asphaltites based on the recent classifications. They can be evaluated as petroleum-derivative resources since the sources are almost alike, considering some rare exceptions. It is noteworthy that although the sources are the same, their characteristics and components are significantly different, which might result from the reactions and processes they go through during their formation. For the

time being, there has yet to be an agreement on the definition of the formation, mechanism, and constituents of bitumens due to the complex structure that asphaltites possess (Hosseini, 2018). However, there is an acknowledged definition suggested by Abraham (1960) used as a basis of all investigations:" Bitumens, in general, are fusible substances, semi-solid or solid, which can be extracted using organic solvents." By the term fusibility, we are determining the temperature at which a material is melted; therefore, by recalling the high fusibility term, we mean that the melting point is low, and so the material tends to melt at a lower temperature. This is defined by comparing the desired substance to the 'reference' one. Another term in this definition is solid or semi-solid, which is commonly specified by the surface or subsurface condition.

2.2.1 Occurance

They are found in similar settings as hydrocarbons and are exposed in veins and vugs in various geological settings (Hosseini, 2018). Therefore, carbonates are the most common geological setting for them; they may also be observed in shale structures, like Dadas formations (Hosseini, 2018).

Bitumens are observed worldwide. They are found in America, especially Utah and the USA, to the most significant extent, followed by western Canada, Argentina, Alberta, and California, as well as southwestern Iran, China, Southeastern Turkey, and so on (Hosseini, 2018). According to the literature, natural bitumen deposits occur in 23 countries, and the resource accumulation is estimated to be 5505 billion barrels of OOIP (Hosseini, 2018). These resources are distributed in 192 heavy oil-containing basins and 89 natural bitumen basins (Meyer and Attasani, 2003; Meyer et al., 2007). In Turkey, bitumens are observed in the southeastern part of the country, such as Şırnak studied by Kavak et al. (2010), where there are many petroleum accumulations; however, solid bitumen veins form the main part of the surficial petroleum occurrences in SE Turkey reported by Lebküchner et al. (1972), amounting to about 82 million tons (Kar, 2006). Bitumens in Turkey also have shown considerable variety in petrophysics and composition compared to the other resources from all over the world, of which being Sulphur-rich and high amount of mineral matter are the most significant factors stated by Hamamci et al. (1997), and they are classified between asphaltite and asphaltic pyrobitumens in terms of composition and as asphaltic pyrobitumens in terms of CS2 solubility (Lebküchner, 1969; Orhun, 1969). Regarding the geological settings,

investigations show that there is a relationship between hydrocarbon occurrences and bitumens in Turkey, as they have a similar carbonate source or marine source (Tosun, 2014).

2.2.2 Formation

According to the literature (Curiale, 1986; Parnell et al., 1993; Rigali and Nagy, 1997; Parnell, 2004), bitumens are derived either by conversion of mineral deposits or petroleum source rocks. If they are the alteration product of organic matters, major processes and factors controlling the formation of the bitumens are a)deposition environment and petroleum composition, b) thermal alteration, c) fluid expulsion and bitumen segregation, and d) biodegradation mentioning that thermal alteration is the primary process in bitumen formation (Hosseini, 2018).

a) **Deposition environment and petroleum composition:** Even though all alteration reactions are regarded as the main factors controlling the production of bitumens, it should be taken into consideration that since they are by-products of petroleum, and the source rocks control the composition of petroleum, other factors are also important. In summary, during the formation of a reservoir rock, different organic materials are merged, resulting in different Kerogen types. These different types of kerogens result in different oils like paraffinic, aromatic, and so on with different compositions and, therefore, different compositional bitumens. Depositional conditions are also important; that is, the fossil type and the mineralogy associated with the conditions they are exposed to, like oxidization, polymerization, etc. An excellent example of that is the Utah basin in the USA (Boden, 2012; Tosun, 2014).

b) **Thermal alteration**: It is regarded as the main process for bitumen formation, especially in Turkey. Two scenarios are considered during thermal alteration: First, the organic-rich source rock forms thermally immature bitumen that migrates a short distance and solidifies in vugs and veins, and second, the petroleum from mature rocks migrates to a relatively prominent destination. This petroleum can form bitumen by thermochemical sulfate reduction or thermochemical reduction. These cases are more frequently encountered in Turkey, giving different compositional bitumens.

c) **Fluid expulsion and bitumen segregation**: This mechanism is suggested to be the factor forming a kind of solid bitumen called 'gilsonite tar ' in the Uinta basin. During this mechanism, in the presence of alkalins, the emulsification of oil-water occurs, and as a result of this emulsification, the interfacial tensions deteriorate. Alongside that, during the fracturing of this reservoir formation, water escapes, and therefore, a combination of this process with other processes like polymerization, etc, simultaneously results in the formation of a kind of solid bitumens called gilsonite as a solid.

d) **Biodegradation of oil** may occur in several ways and locations. By definition, biodegradation is the breakdown of organic matter by microorganisms. This breakdown happens sequentially in oil constituents, beginning with normal alkenes and ending with hopanes, and it can be associated with other processes like oxidation or water-washing, mentioning the second one as an essential factor for forming solid bitumens (Hosseini, 2018). In addition, it occurs with aerobic or anaerobic bacteria in some specific conditions. The alteration that happens in this situation is totally different from that of physical processes since it is the biological alteration of oils in the reservoir (Larter et al., 2006). This kind of bitumen formation usually happens at the water-oil contact since these organisms are abundant and the bio alteration criteria exist.

2.2.3 Physical appearance and characteristics

When talking about asphaltite physical properties, their color may be black, brown, or yellow, and they may be brittle or soft, elastic or plastic as well (Hosseini, 2018). They can be graphitic particles or coatings within the pores of oil or gas-bearing reservoir rocks (Hosseini, 2018). Thus, they are either associated with mineral deposits or are a by-product of petroleum rocks. They can be homogeneous or contain fragments of the current host rock or the rock from which it originated (Cobbold et al., 2014).

2.2.4 Constituents

As mentioned above, the composition of bitumens is not particular to be recognized, resulting from the insufficiency of the tools employed and the composition of bitumens themselves because they are constantly exposed to metamorphosis (Hosseini, 2018).
They can be classified as organic substances containing hydrocarbons and high concentrations of polar compounds containing nitrogen, oxygen, and sulfur (Meyer

and De Witt, 1990). They may be associated with heavy metals such as iron, titanium, molybdenum, vanadium, nickel, and uranium and some polymer-like components (Meyer and Attanasi, 2003; Mossman and Nagy, 2007).

Bitumen's composition is conventionally determined by its solubility in organic solvents (Hunt, 1979). The main components are hydrocarbons bounded by non-hydrocarbon compounds, namely resins, asphaltenes, and pre-asphaltenes, which exist in a tiny fraction (Meyer and De Witt, 1990). The general scheme of this constitution is displayed in Figure 2.1.

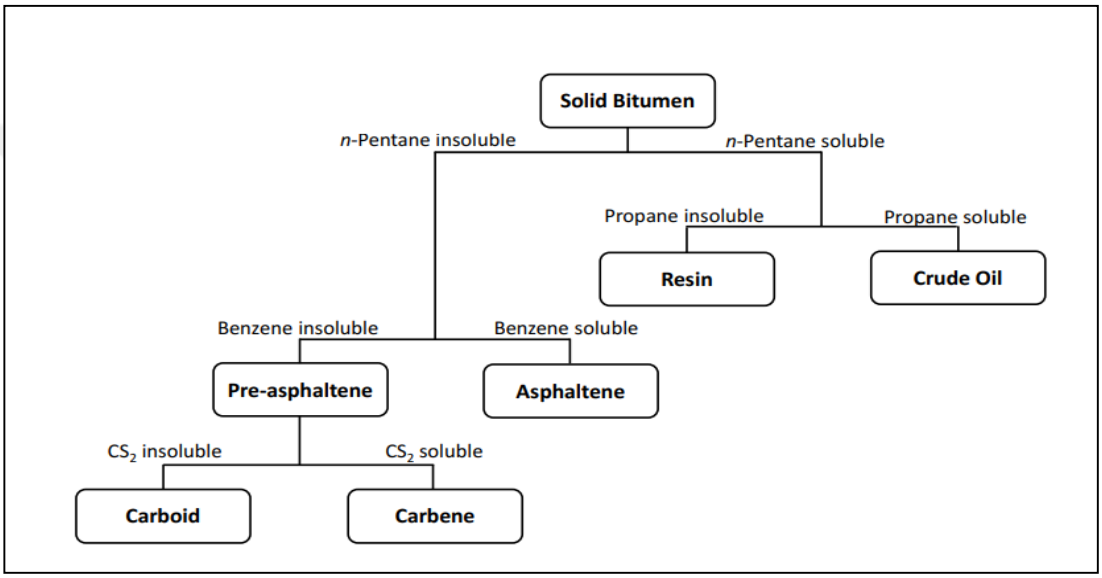

Figure 2.1: Solid bitumen constituted modified by Wen et al. (1978).

When comparing heavy oils in terms of composition, firstly, the C31 homologs of homohopanes, the chemical structure with the general formula C31H54, are more frequent than heavy oil compared to C33 - C35, which is a result of thermal cracking processes. Second, isomers of carbon are more likely to be observed in bitumens, which are due to the expulsion of regular carbon during solidification (Hosseini, 2018). Maturity has a significant impact on the composition of the solid bitumen since it is used to measure many important factors, namely kerogen types(Hosseini, 2018). It is defined as the change in the chemistry of an organic matter contained in a rock, which is functional in determining the amount of hydrocarbon generated by the source. For bitumens, as the study of Hosseini (2018) claims, the maturity series shows the same trend as for shale and coals. Also, less mature bitumens have approximately the same composition as heavy oils, according to this study (Hosseini, 2018).

Bitumens have been proven to be Sulfur-rich in terms of components, particularly in Turkey (Hamamci, 1997). According to the literature, this comes from the mechanism called the deposition environment and petroleum composition combined with thermal alteration in the above sections (Hamamci, 1997). In that phase of formation, if the kerosene Sulphur content is relatively high, then in the TSR process, high-sulfur heavy oils are generated, resulting in an above-average Sulphur rate of bitumens in Turkey (Hosseini, 2018).

2.2.5 Classifications

Several classifications have been proposed for bitumens between 1960 and 1993 based on different physicochemical properties.

Priory, the classification by Abraham (1960) was accepted as a basis, and thereafter, many modifications were proposed, some of which are mentioned in Hosseini (2018). The most commonly accepted and applicable classification in the laboratories is Hunt's (1979) modification of this classification, as shown in Figure 2.2.

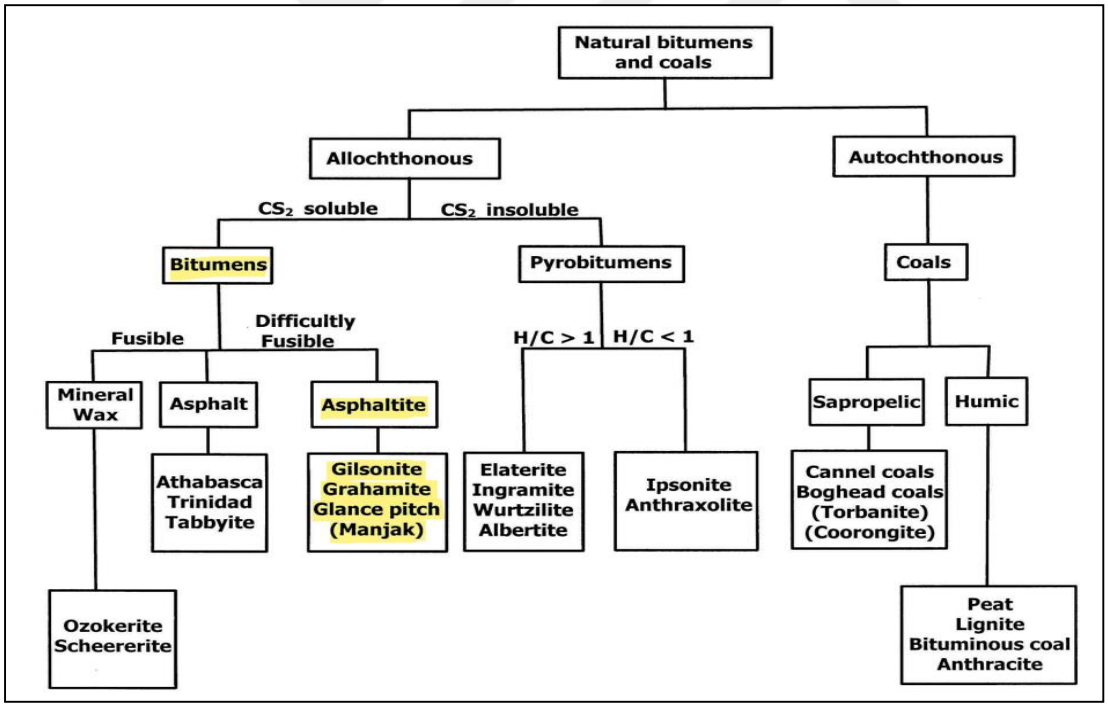

Figure 2.2: Hunt's modification of bitumens' classification (Hunt, 1979).

It is interesting to mention that in this classification, natural bitumens and coals are distinct by the terms called allochthonous and autochthonous, which refer to the location of the materials. If these materials are found in the farther place where they are formed, then they are called allochthonous and vice versa. At this point, based on the formation, they can be distinguished from coals. In some references, natural

bitumen is referred to as solid bitumen, and bitumens and pyrobitumens are called reservoir bitumens (Hosseini, 2018). The term natural in this classification demonstrates the point that this bitumen originated from a source by natural processes, namely thermal alteration, etc., and is not a refinery product.

According to this classification, bitumens are allochthonous organic matters, named as natural bitumens in this classification, soluble in the CS_2, and based on the fusibility, asphaltites are the sub-divisions of bitumen that are difficult to fuse, which means their melting point might be relatively high(>230 °F) and are soluble in CS_2.

Also, in the literature, crude oil is included in this classification in a way that it is classified as allochthonous organic matter distinct from natural bitumen based on its viscosity being lower than 10000 cp.

2.3 Asphaltites

As mentioned above, asphaltites are dark-colored solid petroleum. They are classified as a group of solid allochthonous hydrocarbon bitumens that are soluble in CS_2 and difficult to fuse.

Gilsonites, Grahamites, and Glance Pitches are subdivisions of the asphaltites based on their volatile matter content and reflectivity (Hunt, 1979). Asphaltites are being burned and treated as coal in most of the regions (Hosseini, 2018). Asphaltites have always been a field of interest for researchers due to their extensive implementations in different parts of the industry, and as of the moment, they have become even more significant on account of the rising demand for alternative fuels. In Turkey, especially, petroleum provinces contain asphaltite, therein and as a result, investigation and implementation of these resources are even more critical.

2.3.1 Formation

Asphaltites are extracted either from the naphtabitumen or kerogen. They are formed by alteration during or after the migration and burial during tectonic movements in a way that some reactions such as oxidation, biodegradation, water washing, or maturation take place, causing loss of the light fractions, increase in molecular weight followed by a decrease in the H/C ratio (Hamamci, 1997). They may happen in surface or subsurface conditions in variable geological settings, namely veins, fractures, and sills (Hosseini, 2018). The source rocks may be sandstone, siltstone, claystone, and

anhydrite rocks as well (Hosseini, 2018). They may be associated with oil shale zones and tar sands (cobbold et al., 2014).In the northern part of Turkey, asphaltite resources are formed by intense biodegradation, whereas in the northern part of Turkey, the asphaltites have asphalt origin and are formed either as a by-product of a deeper bituminous level or as a result of upward migration followed by biodegradation (alteration) of oil-bearing zones (Kara-Gulbay and Korkmaz, 2013, 2014).

2.3.2 Occurrence in Turkey

In Turkey, asphaltites are exposed in southeast Turkey in Şırnak, Silopi in Uckardesler, Harbol, and Silip veins and northwestern Gumusacikoy, Northern Turkey (Kara-Gulbay and Korkmaz, 2012, 2013).

Southeastern asphaltite occurrences in Turkey are exposed in the Cudi group, Germav, and Gercus formations (Kara-Gulbay and Korkmaz, 2012). They are either fracture-filling type or fault-exposure, as shown in Figure 2.3.

Silopi asphaltite is classified as a substance between asphaltite and asphaltic pyrobitumen, whereas Şırnak asphaltite is asphaltic pyrobitumen associated with mineral matter (Kara-Gulbay and Korkmaz, 2012; Kavak et al., 2010) The lithification presentative for the asphaltite resources in this area is limestone and dolomites in general, but marl is also observed in the Gercus formation. According to Lebküchner et al. (1972), solid bitumen veins form the main part of the surficial petroleum occurrences in southeastern Turkey, amounting to about 82 million tons (Kar, 2006). Lebküchner (1969) and Orhun (1969) studied Turkey's asphaltite resources and compared them with asphaltic substances from around the world and, as a consequence, classified them as asphaltic pyrobitumens and substances with compositions falling between asphaltite and asphaltic pyrobitumens. Also, it is noteworthy that almost all of the solid bitumens are regarded as asphaltite in Turkish publications (Hosseini, 2018).

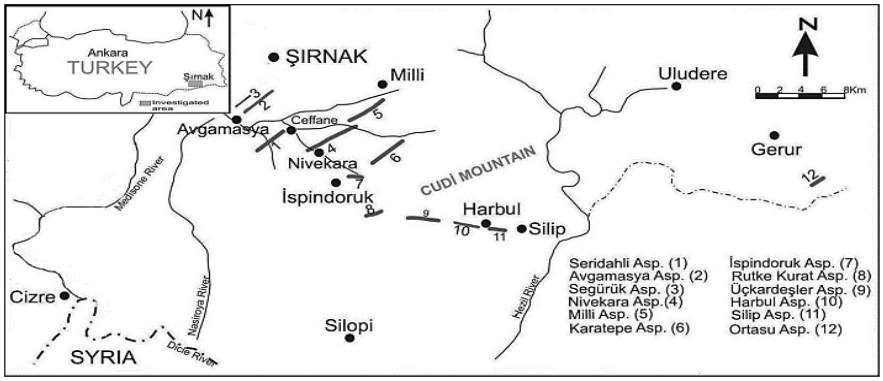

Figure 2.3: Asphaltite distributions in southeastern Turkey (Kara-Gulbay and Korkmaz, 2012).

As shown in Figure 2.4, In the northern part of Turkey, asphaltite resources are found in Gökçukur Plato, Kağnıcı, and Saraycık villages in northwestern Gümüshacıköy, Amasya (Kara-Gulbay and Korkmaz, 2013)

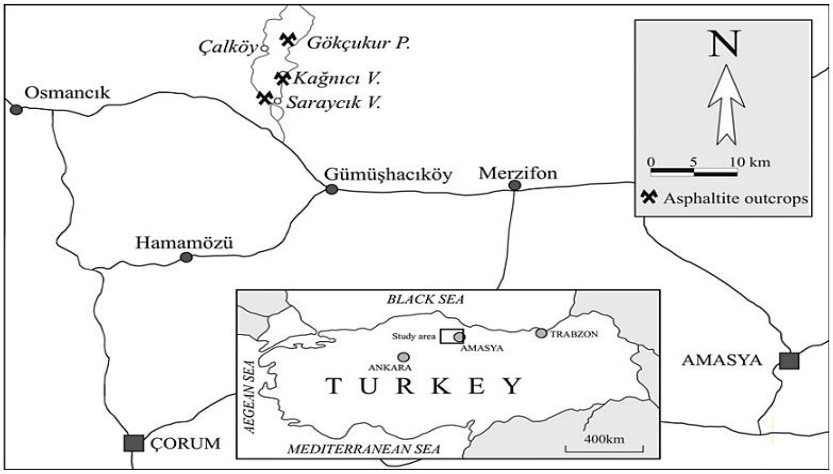

Figure 2.4: Asphaltite distributions in northern Turkey (Kara-Gulbay and Korkmaz, 2013).

The Saraycık asphaltites consist mainly of sandstone, siltstone, claystone, and limestone (Kara-Gulbay and Korkmaz, 2013). The asphaltites are located in the joint systems of this unit and pores of sandstone and siltstone and color in dark gray and black (Kara-Gulbay and Korkmaz, 2013). Kagğnıcı asphaltites have an irregular and patchy distribution within the pores, and they are also the same color as Saraycik. Gökçukur asphaltites are located in the joint systems of this formation, and they do not have comprehensible distribution (Kara-Gulbay and Korkmaz, 2013).

All in all, asphaltites are usually found in veins and fissures (Hosseini, 2018). In order to realize the source rock lithology, carbon isotopes and distribution of normal alkanes, isoprenoids, and biomarkers must be taken into measurement as mentioned in Hosseini (2018), but mainly, in Turkey, the lithology contains at least one unit of solid bitumen except in some rare cases.

2.3.3 Physical appearance and characteristics

They are called black shapeless materials colored as black to dark, comparatively hard, solid bitumens (Hunt, 1979). They are brittle and easily pulverized. Typically, they are low strength, low permeable, and can be highly deformable, and relatively, the cuttability rate is high. They usually have relatively high softening points between 215-

300 °C, and specific gravity ranges from 1.03-1.2 (American Gilsonite Company, 2016). Asphaltite calorific value is significantly higher than the coals due to Asphaltites' tar, benzene, and toluene-xylene contents (Hosseini, 2018).

Regarding Turkey's resources, the moisture content of asphaltites is significantly low; moisture content is the water content per mass of soil or rock, and the volatile matter is almost the same as that of the other coal samples (Tosun, 2014). Also, except for geological settings and procedures, they have shown characteristics as of asphaltic pyrobitumen or something close to them. Solid bitumens in Turkey are Sulphur-rich, and the amounts of associated mineral matter are pretty high (22 to 64%), which is rather unusual for bitumens in general (Tosun, 2014).

2.3.4 Composition

Ashalptites consist of asphaltenes, saturates, aromatics, and polar compounds in different proportions depending on the formation conditions (Meyer and De Witt, 1990). They are composed of hydrocarbons with almost no oxygenated compounds and crystallized paraffins (Hunt, 1979). Alkenes in the range of C13-C31 are the most abundant in the asphaltites, and in general, they consist of <C18 and low-numbered alkanes are not or almost non-existent (Hosseini, 2018).

Compared to the coals, ash content and sulfur content are almost doubled, which is a result of clay minerals, quartz, albite, orthoclase, pyrite, calcite, dolomite, Mo, V, Ni, Ti, Al, Si, Fe, Cu, Ca, U, etc called as trace metals in the literature (Mossman and Nagy, 1996; Attanasi and Meyer, 2010; Clapp, 1917). Natural asphaltites contain 1–5.3% (wt.) total moisture, 33–45% ash, 4.1–6.4% sulfur, 24–40% volatile matter, 47–59% fixed carbon,3.2–5.6% hydrogen and soluble in CS_2 98-100% (Tsyntsarski et al., 2013).

The asphaltites in northern Turkey show similar compositions in saturated and aromatic carbon, isotropic strain distributions, and fractions of C27, C28, and C29 (Kara-Gulbay and Korkmaz, 2013). Alkenes in the range of C19-C26 are the most abundant in asphaltites, and in general, low-numbered alkanes are not or are almost non-existent (Kara-Gulbay and Korkmaz, 2013).

All in all, it can be stated that the determination of the contents of the asphaltites depends highly on the exposure of these resources, the alteration and the degree of the alteration they have been subjected to, the maturity level of asphaltites, and the source rock they are contained in as stated in Hosseini (2018). For example, if asphaltite is

exposed to wide fractures, organic carbons are higher, and different hydrogen content is due to the various degrees of biodegradation and the environment (Hosseini, 2018). The homohopane distributions of these resources are roughly different in some chains (Hosseini, 2018).

Last but not least, all of the asphaltite occurrences in northern Turkey have been proven to be from the same source rock and have been formed from the same origin (Kara-Gulbay and Korkmaz, 2013). Asphaltite occurrences in the southeastern part of Turkey contain high amounts of ash and Sulphur, and their calorific value is high, as mentioned before (Hamamci, 1997). Compared to the oils from the same locations in the first investigations, they seem to show similar characteristics in terms of composition, so their origin was concluded to be the same, but according to Tonbul (2006), they haven't originated from the same oils associated with asphaltites in some locations, and the debate still continues.

Investigations into the southeastern resources of Turkey show that the organic carbon level varies dramatically in different locations due to the processes that the host rock is subjected to, like bitumen invasion (Kara-Gulbay and Korkmaz, 2012; Kavak et al., 2010). Also, in this region, the hydrogen index is relatively high in contrast to the oxygen index, which shows N-alkanes existence and a low level of biodegradation (Kara-Gulbay and Korkmaz, 2012). Carbon isotopic values are similar, but they are not representative of organic matter (Hosseini, 2018). Since the effect of the carbonates combined with other investigations, it can be concluded that the asphaltites are from the same genetic family of origin and formation structure (Kara-Gulbay and Korkmaz, 2012).

Regarding the gas contents of asphaltites, nitrogen, carbon dioxide, methane, ethane, propane isobutane, n-butane isopentane, and n-pentane exist in the asphaltite in different proportions (Hosseini, 2018). It is evident that the gas content decreases with the increase in the depth of the reserve.

2.3.5 Subdivisions

According to the reference classification, Gilsonite, Grahamite, and glance pitch are subdivisions of asphaltite (Hunt, 1979).

Table 2.1: asphaltite categorization based on fixed carbon number (Kelso and Powell, 1944).

Asphaltite	Fixed Carbon,%
Gilsonite	10-20%
Glance pitch	20-30%
Grahamite	30-55%

They can be characterized by several characteristics like softening point, specific gravity, and so on but the most common categorizing is by the carbon number. Their approximate characteristics are given in Figure 2.5.

Properties	Gilsonite®	Glance Pitch	Grahamite	Natural Asphalt
Specific gravity @77°F	1.01-1.04	1.10-1.15	1.12-1.50	1.4-1.45
Softening point	>300°F	270-375°F	350-600°F	>250°F
Soluble in CS_2	>99%	>95%	45-100%	56-67%
Inorganic or mineral matter	0.3%	5%	up to 50%	36.9%
Fixed carbon	<20%	20-30%	>30%	10.8-12%
Carbon content	89.28%	80.87%	86.56%	82.33%
Hydrogen content	8.66%	10.42%	8.68%	10.69%
Sulphur content	<1%	9.52%	1.79%	6.56%

Figure 2.5: Asphaltite types and specifications (American Gilsonite Company, 2016).

Characterizing asphaltites based on the carbon number is the most common one (Kelso and Powell, 1944). Based on fixed carbon numbers shown in table 2.1, studied by Kelso and Powell (1944), fixed carbon changes from 10 to 55%, with Gilsonite as the lowest and Grahamite as the highest carbon.

2.3.5.1 Gilsonite

As can be seen in Table 2.1, if the asphaltite's fixed carbon is less than 20%, it is gilsonite. According to Hunt (1979), the normal range of fixed carbon is 13-18.6% in gilsonites. Gilsonite is the subdivision most frequently discussed in the literature. Gilsonites are asphaltite deposits found in the Uintah basin at the largest extent(Hunt, 1979). Since gilsonite has been produced there for a long time, comprehensive investigations and research are available on them. Gilsonites are observed in fractures, veins, or as distributed points in larger minerals contained (Hunt, 1979). They are shiny black or black, with conchoidal to columnar (penciled) to flaky or scaly fractures (Boden and Tripp, 2012). Their specific gravity varies between 1.01-1.1 g/cc, and their solubility in CS_2 is 98% (Abraham, 1960). They are formed in various structures, from

carbonates to shales, and in some cases in sandstones and siltstones, and can be exposed primarily on veins and fractures and, in some minor cases, in faults (Boden and Tripp, 2012). In many investigations, they are believed to have originated from kerogen-rich oil shale zones, and then, by tectonic movements and regional stresses, they are solidified in the fractures. The detailed formation mechanism of gilsonites is discussed in previous sections. In terms of their exploration, there is yet no accurate method that can be regarded as a reference, but the latest developments, such as electrical resistivity imaging and electrode spacing methods used in Boleneus (2007), seem to be a significant contribution. Also, the mining techniques of these resources highly depend on the vein's width.

2.3.5.2 Glance Pitch

Glance pitch is a black, shiny, conchoidal fracture surface type of asphaltite that is characterized as an intermediate between Gilsonites and Grahamites(American Gilsonite Company, 2016). Its fixed carbon ranged between 20-30%, specific gravity of 1.1-1.15 g/cm, and CS_2 solubility of 97-100% (Kleso and Powell, 1944; American Gilsonite Company, 2016). They are called 'manjack,' too, and they are mainly found in Barbados but also in some other reserves, such as Haiti, Cuba, Mexico, the United States, Argentina, and Colombia (Demirci et al., 2019).

2.3.5.3 Grahamite

Grahamite is a very black, shiny type of asphaltite that is characterized by its fixed carbon ranging between 30-55%, the specific gravity of 1.1-1.2 g/cm, and CS_2 solubility of 90-100%, and has the highest softening points among all other its relatives (Demirci et al., 2019). They are found in Cuba, Mexico, West Virginia, and Oklahoma, United States (Demirci et al., 2019).

2.4 Asphaltite Gasification

In today's world of increasing population, there always emerges a struggle to provide energy; thus, there comes the idea of alternative fuel to supply this demand. Asphaltites are one of these prominent alternatives. Since there are environmental issues concerned with the direct implementation of these resources for electricity production, such as CO_2 emissions and high Sulphur contents, alternative methods for utilization

of asphaltites should be investigated. Among those methods, gasification is reviewed briefly in this literature review.

The asphaltite gasification process is almost like coal gasification, and even in some literature, Turkey's asphaltites are regarded as coal. In this process, briefly, a vertical furnace containing coal and flue gas is used, and after the gasification, the oil yield varies between 22-28%, of which 15-20% are low-boiling fractions. Also, some water contamination may be caused, which needs to be considered. Afterward, the gaseous product is analyzed and can be subjected to desulphurization processes for further applications.

Every solid gasification proceeds in a so-called "two-step" experiment, first pyrolysis and then gasification. In the pyrolysis step, the volatile contents are released at a lower temperature, and then the residues are subjected to gasification.

The general procedure for the gasification of asphaltite is as follows: The experiment setup usually consists of a furnace, a rector, injectors, thermocouples, condensers, filters, ash, and sample collectors. Also, temperature, gas emission, gas chromatography, and mass flow monitoring systems are always synced with the setup. Firstly, the samples are crushed by controlled screening, and then desired amounts of these samples are taken and sealed in nylon bags. In the next step, particle size distributions and specific surfaces are measured to consider whether they can react adequately with the reactants. Then, the samples are placed in the fluidized-bed reactor. The reactor's durability should be high enough because asphaltites' gasification occurs in high temperatures in the range of 600-1100 °C. The furnace provides the heat, and the reactor is placed into the furnace typically, coupled with the thermocouples, which measure the temperature of the reaction consistently.

During the experiment, nitrogen, air, oxygen, and carbon dioxide can be injected into the reactor simultaneously or periodically, depending on the purpose of the research. After the gasification is finished, the gas passes through the set filtrates, and after crossing over the condenser in order to cool down, the desired operational data is collected for further analysis. Conventionally, hydrogen, methane, and hydrogen sulfide fractions of the gas are measured by the gas analyzer. The gaseous product, eventually, is deployed in several industries like electricity, petroleum, etc., or further research.

Compared to coals, as approved, asphaltites show dramatic calorific value during the gasification process, while the gaseous, oil, and ash products are relatively the same.

(Tosun, 2013) As mentioned before, this high calorific value comes from the tar, benzene, toluene, and xylene fractions in unit process gas.

It is apparent that the gasification process has environmental benefits. First of all, fossil fuel resources contain carbon. These resources are primarily used in power and heat production by combustion, which could be more efficient. Therefore, by means of gasification, the syngas produced can be refined and utilized better.

Also, these resources cause hazardous emissions of carbon dioxide, carbon monoxide, and hydrogen sulfide if extracted directly or combusted due to their heavy and complex components, such as tars, ash, or sulfur. By means of gasification, these hazardous emissions are prevented, and a cleaner gaseous product is produced.

Thirdly, compared to burning, carbon and water contaminants are almost non-existent.

Lastly, if this process can be managed underground, more advantages are achieved: the gases produced can be recycled to the reserve for enhanced recovery purposes, the reserve itself may provide some gases for the gasification process to take place more rapidly, and the emissions, if any, are released underground and are no longer a threat to the environment. Also, produced ash would reside underground.

In other words, despite all of the advantages and conveniences of this method listed earlier, there need to be more investigations and research; therefore, it can not be well-developed and deployed all over the world.

2.5 Summary

In this literature review, the characteristics, origin, formation, occurrence, and categorization of asphaltites are investigated thoroughly. Reviewing the literature suggests that there needs to be more clarity about the exact definition of asphaltites and their characteristics all over the world as they tend to show completely different compositions in various resources. Since asphaltites are abundant in Turkey, particularly in the southern part, and they have widespread application in industries such as power generation, all of the mentioned points are reviewed for Turkey's resources also. It is recognized that Turkey’s asphaltite differs from other resources in the world due to its high sulfur and ash contents. Moreover, because of the problems associated with the direct implementation of asphaltites, gasification can be a cleaner alternative method of asphaltite extraction. Reviewing the literature regarding the gasification of asphaltites shows that there are almost no or some rare

studies investigating this process in Turkey. Therefore, this study aims to investigate the kinetics of the gasification process of asphaltites in order to get a better understanding of the mechanism of gasification, probable reaction series, heating rates, effluent gas concentrations, as well as their conversion during gasification, and kinetic parameters through the isconversional method analysis.

3. METHODS AND MATERIALS

This section covers all necessary information on conducting experiments on asphaltites and coal kinetic-cell combustion.

First, the apparatus and samples are explained. Then, the system and reactor setup, calibrations, and all the necessary points that need to be taken into consideration are described. Then, in the last step, the experimental procedure is covered, and the overall information of all experiments conducted is given.

3.1 Experimental Work Overview

As a general overview, coal and asphaltite samples go over combustion in a kinetic-cell reactor in these experimental sets. In order to do that, the air is injected into the system with a fixed pressure and flow rate. During the experiments, temperature, pressure, flow rate, and concentrations of effluent gases are measured and monitored continuously. Once the gas is produced, it passes through liquid and sand filters and gas purifiers. Once the target heating rate is reached, the system turns off automatically, and the raw data, consisting of effluent gas concentrations and temperature with respect to time, is saved on the computer connected to the system.
In total, nine experiments were conducted on coal and asphaltite samples. The details of the samples and the amounts will be mentioned later. Out of 9 experiments, four were conducted on asphaltite, and five were conducted on coal samples with different heating rates, details of which will be given in this section.

3.1 Experiment Equipment

This section explains the tools used ure for monitoring, measuring, controlling, and logging the parameters in the experiment procedure.

3.1.1 Reactor

The reactor is a stainless cylindrical tube reactor with a 2 cm wall thickness and a 14.5 cm kinetic cell. The thick wall thickness ensures that the high temperature is durable and sustainable during the experiments.

The reactor consists of top and bottom flanges, each with six screw holes on it, thermocouple, gas, and liquid inlets, and outlets, as well as a pre-heating coil fixed on the bottom flange, as can be seen in Figure 3.1. In order to prevent any leakage, a copper gasket is put between the wall and the top and bottom flanges of the reactor.

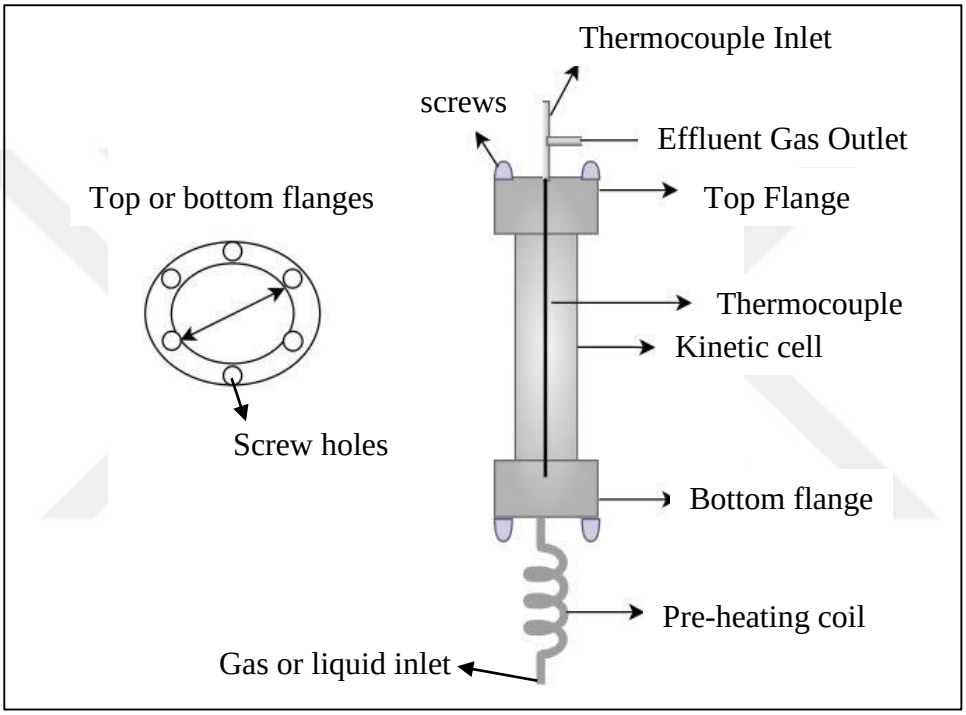

Figure 3.1: Reactor (kinetic cell) schematic.

3.1.2 Thermocouples

K-type and J-type thermocouples are used in these sets of experiments. A total of 4 thermocouples are used to track the temperature and also ensure the consistency and uniformity of temperature continuously during the gasification process. A j-type thermocouple with three logger plugs is placed in the kinetic cell so that the bottom, top, and center of the reactor's temperature can be measured. 3 K-type thermocouples are placed inside and outside the furnace to control the reactor wall and furnace temperature, and the other one is placed in a way that can control the ambient temperature. K-type thermocouples can tolerate a maximum temperature of 1260 ºC with an accuracy rate of 0.04 percent, while j-type thermocouples can tolerate a

maximum temperature of 760 ºC with the same accuracy rate (Thermocouple Info, n.d).

3.1.3 Measuring and monitoring tools for temperature

Temperature controller, reader, limit controller, and loggers are the measurement and monitoring tools used in this set of experiments.

3.1.3.1 Temperature logger

Thermocouples are directly connected to a data logger provided by MCC (Measurement Computing Corporation), which is connected to the PC via USB-TC, allowing it to measure the temperature in seconds by means of TracerDAQ.

The USB-TC device has eight inputs and outputs for thermocouples and can be connected to the PC via a USB cable (Measurement Computing Corporation, n.d.). Instacal software allows the calibration of thermocouples and temperature testing before starting the experiments (Measurement Computing Corporation, n.d.). TracerDAQ is a data acquisition program that allows temperature tracking per second, and the results are recorded in an Excel file once the experiment is finished (Measurement Computing Corporation. (n.d.).

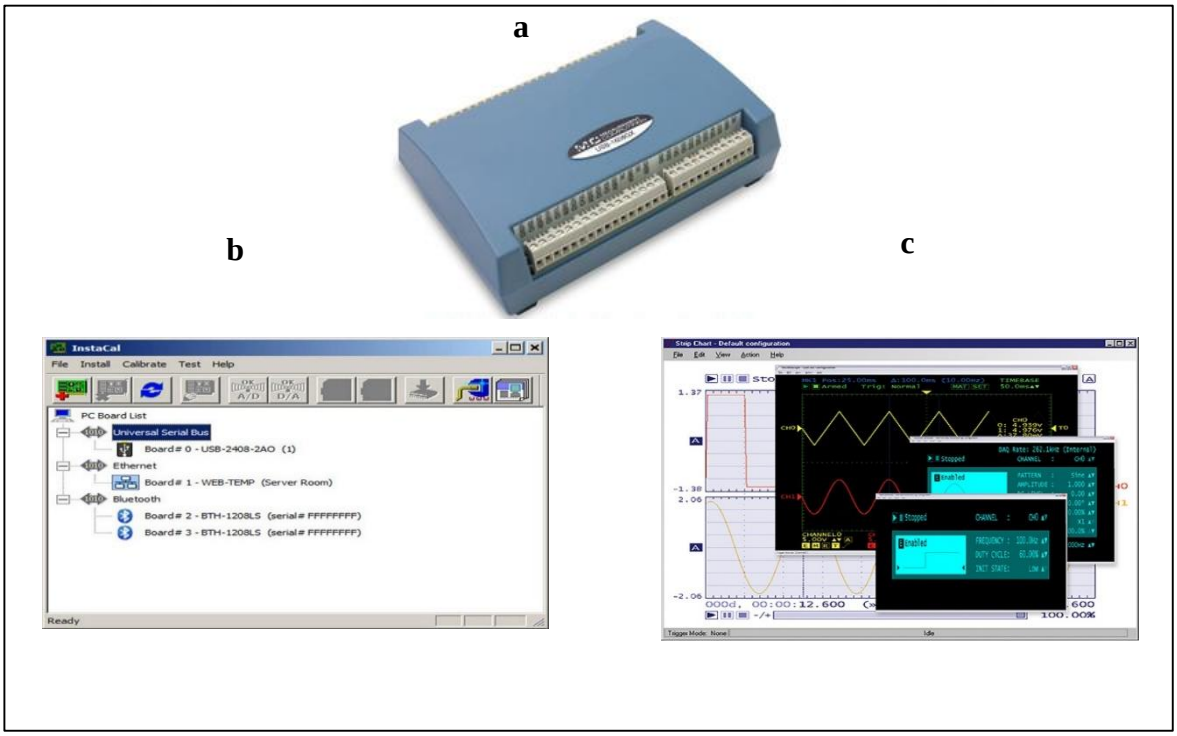

Figure 3.2: Temperature logger tools: a) USB-TC, b) Instacal,& c) TreacerDAQ.

3.1.3.2 Temperature controller

To perform these experiments, different heating rates must be applied to the system. Omega model CN8201 series, temperature controller shown in Figure 3.3, does this. Before starting each experiment, the target temperature, in this case, a maximum of 650 ºc, is set through the controller. The ramp and soak option is chosen for heating. In this method, in addition to the target temperature, the time needed for the system to reach that temperature is also entered into the device. The temperature controller works based on the furnace temperature, and when the target temperature is reached, it is set on standby mode automatically.

Figure 3.3: Tempreture controller.

3.1.3.3 Temperature limit controller

Temperature limit controllers are set to shut down the system if the temperature controller fails to work properly (Omega Engineering, Inc., n.d.). They work on the basis of controlling the thermocouple temperature, which is set in the furnace, and ensure the safety of the experiments. The model used in these sets of experiments is the Omega CN3261 series, shown in Figure 3.4.

Figure 3.4: Temperature limit controller.

3.1.3.4 Temperature reader

The temperature reader is a thermometer that reads the temperature of the furnace. The model used in this series of experiments is from Omega Engineering products model 2176A, as can be seen in Figure 3.5.

Figure 3.5: Temperature reader.

3.1.4 Mass flow controller

A mass flow controller is used to observe the supply and production flow rates in the system. The flow should be consistent and pre-determined during the experiment; therefore, flow rate controllers allow us to observe and ensure it. The model used in this set of experiments is from Brooks Instruments series 0250 model 0254, which can be seen in Figure 3.6. Through these, the controller's display settings are done, and readings are observed (Brooks Instrument, n.d.).

Figure 3.6: Mass clow controller.

3.1.5 Gas analyzer

The gas analyzer is the most important device in this set of experiments. It measures the composition of the produced gases, namely O_2, CO_2, CH_4, and CO, as shown in Figure 3.7.

The model used is Servopro 4200 from Servomex company. It measures O2 through a paramagnetic sensor and the other gases with infrared sensors through a stream of gas (Servomex, n.d.).

To use the gas analyzer, both high and low calibration should be performed before each experiment. Then, during the experiment, using Hyperterminal software, the composition of the syngas is recorded continuously, and when each experiment is finished, the data is captured as a text file instantly.

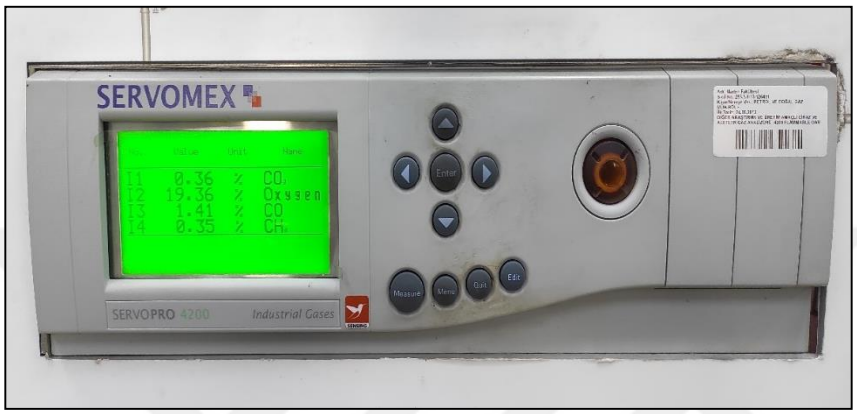

Figure 3.7: Gas analyzer.

3.1.6 Pressure gauges

A number of pressure gauges are set in the system to control, measure, and observe pressure during the experiments. Pressure gauges show the supply tank, cell inlet, line, cell outlet, and the pressure of the gas entering the gas analyzer, respectively.

3.1.7 Filters

Liquid traps, sand filters, different micrometer particle filters, and gas purifiers are the filter types used in kinetic cell setup systems.

The first filtering stage occurs when the Air tank supplies the system. At this stage, 2µ and 7 µ filtering is applied to air particles. Thereafter, three filter stages will be employed for the gas coming out of the cell during the experiment.

First and foremost, clearly, because the temperature of the gas coming out of the cell is too high, the gas should be cooled down and condensed, and therefore, the liquid content should be filtered using the liquid trap. In the following step, the gas passes through a cylindrical tube of sand filtrate in order to ensure there is no contamination of solids in the system. At the last stage, a gas purifier is placed in a system to filter the probable remaining hydrocarbon, water, particles, etc. Then, before the vent, it

again passes the 7 µ filter. Some of the filter apparatus is cleaned after each run, if necessary, depending on the impurity of the sample, time of the experiment, homogeneity of the environment, and other parameters.

3.2 Experimental Setup and Procedure

This section covers the steps that should be taken for procedures related to initialization and the progress of the experiments.

3.2.1 Implemented samples

The details of the samples and the samples used in this set of experiments can be seen in Table 3.1 and Figure 3.8. The coal sample was provided from Soma, and the Asphaltite sample was taken from Şırnak in the southeastern part of Turkey.

The amount of the sample chosen for the experiment should be selected in a way that guarantees logical values of concentrations for analysis, avoids temperature failure in the gasification procedure, and is determined by trial and error.

Table 3.1: Details of Samples Used in the Study.

Sample	Sample	Amount
Coal	Soma	1.5 gr
Asfaltite	Şırnak	2 gr

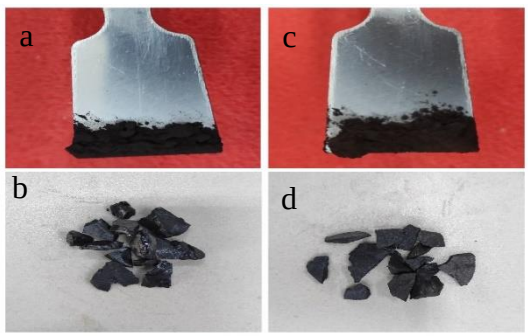

Figure 3.8: a,b) Coal sample; c,d) Asphaltite sample.

3.2.2 Reactor setup

Before setting up the reactor, the sample should be prepared. Firstly, they are crushed into small pieces as shown in Figure 3.8 b and Figure 3.8 d, and then they are powdered using Pulverisette 9 like in Figure 3.8 a and Figure 3.8 c. It is better if the sample is prepared right before the experiment each time since, in this way, any probable reaction with the atmosphere will be avoided.

To prepare the reactor, the flanges should first be connected and fixed. It is recommended that the flanges be fixed parallel, as shown in Figure. 3.1 to ensure there will be no misplacement in any case. The schematic of the assembled reactor is shown in Figure 3.9. In this way, a mesh is placed at the bottom of the reactor to prevent any possible intrusion and vent. Thereafter, 45 gr of coarse sand is measured and placed into the reactor. Eventually, 50 gr fine sand is well mixed with the sample to dilute the sample and then put into the reactor. After that, the top flanges of the reactor are connected using a copper gasket in between the reactor and the top flanges. In the last step, the thermocouple is fixed into the thermo probe of the reactor just as it can measure the temperature of the top, bottom, and center of the cell, respectively.

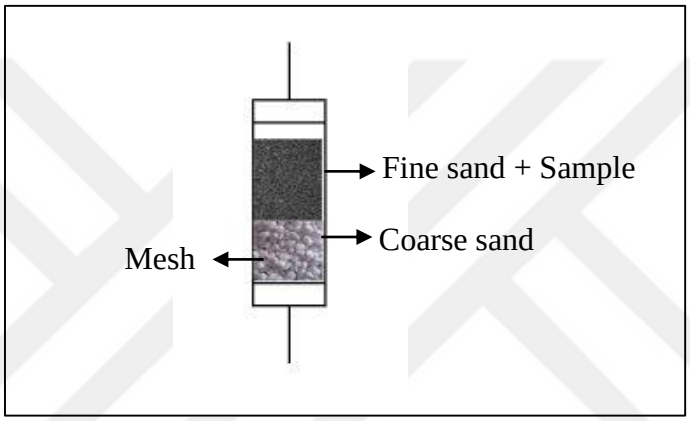

Figure 3.9: Prepared reactor schematic.

Before placing the reactor in the furnace and connecting it to the system, a leakage test must be performed with a foamy solution and by pressurizing the system provided by the Air Tank to ensure it is completely sealed.

3.2.3 System setup

Figure 3.10 shows the schematics of the experiment's system. After preparing the reactor, it is placed in the furnace. Then, the bottom coiling tube is connected to the Air tank since the oxidant in this set of experiments is Air. The top flanges of the reactor are connected to a 1/4 tubing line. This helps reduce the high-temperature gas coming out of the reactor as a result of the combustion process.

Consequently, liquid trap, sand trap, and gas purifier are connected to the system to ensure the 3-stage complete filtration. The system is followed by a relief valve placed at the bottom of it to prevent any possible liquid contamination in the system. There is also another relief valve set before the gas analyzer. This valve helps the system reach consistency and ensures that the rate flowing in the gas analyzer does not exceed its

maximum limits. Besides, since the pressure of the gas entering the gas analyzer must not exceed 4-5 psi in case of any failure in the instrument and data measurement, a pressure gauge is placed before the gas purifier, which allows the conductor to control and, if necessary, note the pressure of the released syngas occasionally.

After this system is set, thermocouples are placed in the reactor, furnace, inner part of the furnace, and the atmosphere. They are connected to the temperature reader, controller, and PC so that they can record the temperature data simultaneously. The data measurement frequency in this set of experiments for temperature is every second.

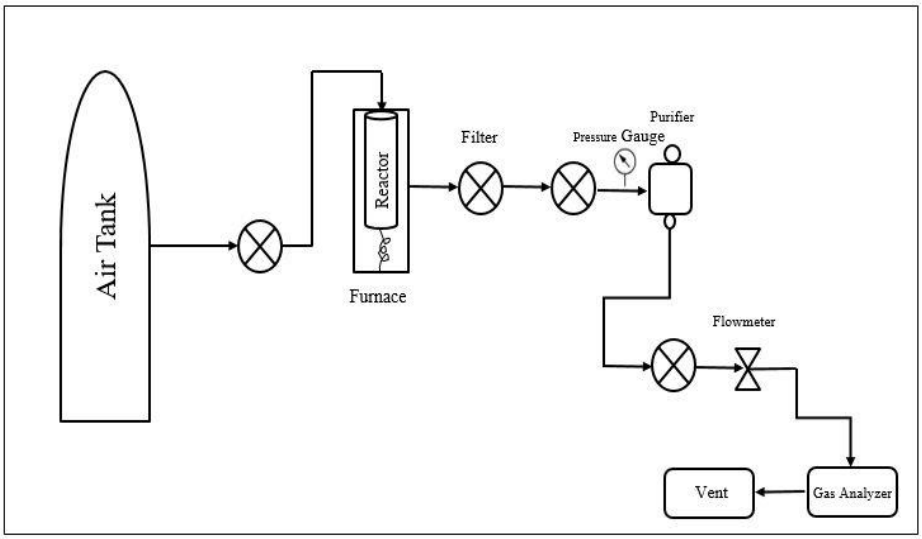

Figure 3.10: Experiment system.

3.2.4 System calibration

Before initializing the experiments, the system should be calibrated. There are three calibrations that should be performed on the system: 1. Gas analyzer 2. Thermocouples

Two calibrations should be performed on the gas analyzer, low and high calibration. Low calibrations are done under the flow of the Nitrogen valve and all the flowing system's effluent gases namely, CO, CO_2, CH_4, and O_2 should be calibrated to 0.00 % concentration at this stage. Then, all modules are high calibrated using the appropriate tanks.

The last step is the calibration of thermocouples, they should be first tested and then calibrated. To test the thermocouples, Instacal software is used and all the port temperatures are measured by the temperature logger connected to a computer and shown on the display screen consequently. Then, after checking all temperature ports

set to atmosphere temperature, thermocouples are calibrated automatically using the software.

3.2.5 Experimental procedure

To start the experiment, the temperature controller is used to impose a target heating rate. Then, the air tank valve is opened, the furnace is turned on, and temperature monitoring tools are plugged in.

Throughout the experiment, air first enters the pre-heating coil in order for its temperature to increase to the applicable combustion temperature. Thereafter, the temperature rises gradually, and the air flows in the cell, and combustion reactions occur step by step. After the produced syngas gas pressure is controlled, the gas passes through the filter steps, and thereafter, the concentration of the produced syngas is measured by the gas analyzer. It should be noted that concentrations of the effluent gas, pressures, namely cell, system, tank inlet and outlet, flowmeter, and temperature data, are recorded simultaneously per second and either saved into the PC connected to the setup system or displayed on the screen of each apparatus. Instantly after the target heating rate is reached, the temperature controller automatically shifts to standby mode so that there will not be any temperature increase in the system. Thereafter, the furnace, temperature controller, and reader are plugged off, and the whole system is turned off and cooled down until the next day.

Some points should be considered before each experiment, which are as follows :

- The reactor and filters should be unscrewed, cleaned, and dried separately to avoid any contamination, leakage, or error in the following experiment. The cleaning procedure is done using Toluene and allowable detergents and all the pieces are dried in a desiccator cabinet consequently.
- The reactor and the furnace should cool down to the atmosphere temperature. If necessary, a cooler can be used.
- All of the thermocouples should be calibrated to the atmosphere temperature.
- All the calibrations mentioned in the previous section should be taken care of.

3.3 Overall Experiment Information

A total of 9 experiments were conducted on samples with different heating rates, details of which are mentioned in Table 3.2.

Table 3.2: Experiment information.

Sample	Number of Experiments	Heating Rates (ºC/min)
Coal	5	2.71, 2.41, 2.20, 2.00, 1.80
Asfaltite	4	2.71, 2.20, 2.00, 1.80

Of course, other experiments were conducted; nevertheless, they led to system malfunction due to different technical or human mistakes, such as thermocouple misplacement, data logger tool failure, or interruptions.

3.4 CMG SIMULATION

In the last step of the analysis, CMG's STARS module is used to simulate the gasification of coal samples at different heating rates. As understood previously, gasification involves a complicated, parallel series of chemical reactions; thus, using a commercial simulator would be a good help firstly to verify the experimental results and also to get an idea of the process scheme and its optimization. By carrying out the simulation, it is possible to realize the combustion process. Besides, it contributes to a better understanding of the observed changes in temperature and effluent gas concentrations. This is performed to see if the experimental and simulation results match and validate each other.

STARS simulates the thermal and advanced processes of oil and gas reservoirs. STARS is more favorable since it helps to optimize the plans and well designs for thermal chemical EOR processes, which contain steam distribution and complex component injections at different scales and is most favorable in the case of in situ combustions (Stars Solution, n.d).

STARS is a preferred tool for modeling the gasification of coal due to its comprehensive and robust capabilities. Firstly, it excels in simulating complex thermal and chemical processes, which is critical for accurately modeling the intricate reactions involved in coal gasification, including pyrolysis, oxidation, and reduction. It also ensures the understanding of the reaction mechanisms, which is essential for optimizing the gasification process. This module also guarantees the handling of heat and mass transfer, which is crucial for representing temperature gradients and heat flux involved in the gasification process. Additionally, the software's tools for integrating

experimental data facilitate detailed analysis and validation of simulation results against real data, ensuring high accuracy and reliability.

3.4.1 Model configuration, properties, and initial conditions

As can be seen in Figure 3.11, the model is a one-dimensional 4-layer radial reservoir. This model simulates the kinetic cell and furnace system in that the first and second layers resemble the kinetic cell and its wall, the third layer is the space between the furnace and the kinetic cell, and the fourth layer is the furnace.

Table 3.3 shows the properties assigned to each layer, namely porosity, initial saturations and concentrations, initial pressure, and temperature. The porosity is considered zero in the second and fourth layers because these represent the reactor wall and furnace. Also, the first layer's initial saturation values are valid, so the other layers' values are considered zero.

Since the permeability effects will not be discussed in this study, they are assumed to be very high. Also, for the sake of simplicity, complex multi-dimensional models are not used in this simulation.

Table 3.3: Reactor model properties.

Property	Value	Property	Value
Permeability	30000 md	Initial Temperature	25 ºc
Porosity	0.38	Water Saturation	0.25
Surface Temperature	20 ºc	Liquid Saturation	0.1
Surface Pressure	101.325 Kpa	Gas Saturation	0.65
Initial O2 Concentration	0.2073	Initial N2 Concentration	0.7927
Operation Pressure	689.5 Kpa	Initial Coal Concentration	0.044
Initial Pressure	689.5 Kpa		

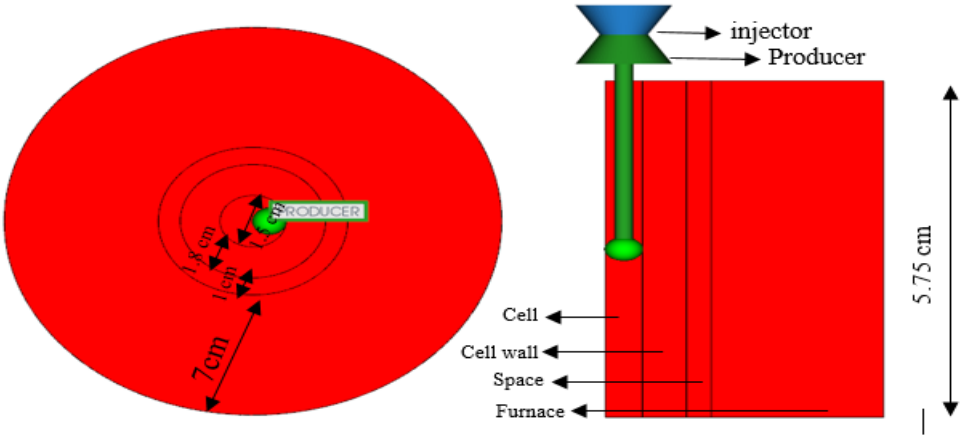

Figure 3.11: CMG model dimensions and layers.

3.4.2 Reactions

One of the most important steps in simulating the coal gasification process is determining the reactions involved. As a matter of fact, every gasification process consists of two steps: pyrolysis and gasification itself. In the pyrolysis stage, coal undergoes a reaction that results in the release of volatile matter and solid matter. Consequently, the solid matter is subjected to gasification. The pyrolysis reaction and reaction series used in this study as input data are obtained from the study of Nourozieh et al. (2010) and listed as equations 3.1 to 3.8.

$$\text{Coal} \rightarrow 4.63\text{Carbon} + 0{:}43\text{CO} + 0.12\text{CO2} + 0{:}79\text{CH4} + 0.18\text{H2} \quad \textbf{(3.1)}$$

$$\text{C} + \text{O2} \rightarrow \text{CO2} \quad \textbf{(3.2)}$$

$$\text{C} + \text{CO2} \rightarrow 2\text{CO} \quad \textbf{(3.3)}$$

$$\text{C} + \text{H2O} \rightarrow \text{H2} + \text{CO} \quad \textbf{(3.4)}$$

$$\text{C} + 2\text{H2} \rightarrow \text{CH4} \quad \textbf{(3.5)}$$

$$\text{CO} + \tfrac{1}{2}\ \text{O2} \rightarrow \text{CO2} \quad \textbf{(3.6)}$$

$$\text{CO} + \text{H2O} \leftrightarrow \text{CO2} + \text{H2} \quad \textbf{(3.7)}$$

$$\text{CH4} + \text{H2O} \leftrightarrow \text{CO} + 3\text{H2} \quad \textbf{(3.8)}$$

The kinetic parameters such as activation energy, enthalpies, and frequency factors are obtained from the study of Norouzieh et al. (2010) and estimated and regularly optimized depending on the conditions of the reservoir, which can be seen in Table 3.4.

Table 3.4: Kinetic parameters.

Reaction	Activation Energy[kj/mole]	Enthalpy [kj/mole]	Frequency Factor
Pyrolysis (5.1)	0	0	$4*10^{13}$
Oxidation (5.2)	60	-130	400
Boundary (5.3)	249	172	$13*10^{6}$
Steam gasification (5.4)	156	131	$4*10^{4}$
Hydrogenation (5.5)	200	-75	$4*10^{3}$
Carbon Monoxide Combustion (5.6)	247	-566	$2.2*10^{8}$
Gas-steam shift forward (5.7)	12.6	-41	3.5
Gas-steam shift backward (5.7)	12.6	41	0.1
Methane-steam reforming forward (5.8)	30	206	600
Methane-steam reforming backward (5.8)	30	206	$8*10^{3}$

3.4.3 Operational Conditions

The next step is to clarify the furnace and impose the heating rates in desired temperatures. To do so, first, the furnace is situated in the 4th layer, then the constant heating rate is determined and eventually, the temperature increase each time, coming from the experimental raw data, is imposed on the system.

Temperature propagation during the experiment with a heating rate of 2 ºC/ min at the start, after 2.30th hours, and at the end of the experiment is shown as an example in Figure 3.12. Accordingly, as shown in Figure 3.11, an injector and producer well should be defined in the system, constraints and operational conditions of which are tabulated in Table 3.5.

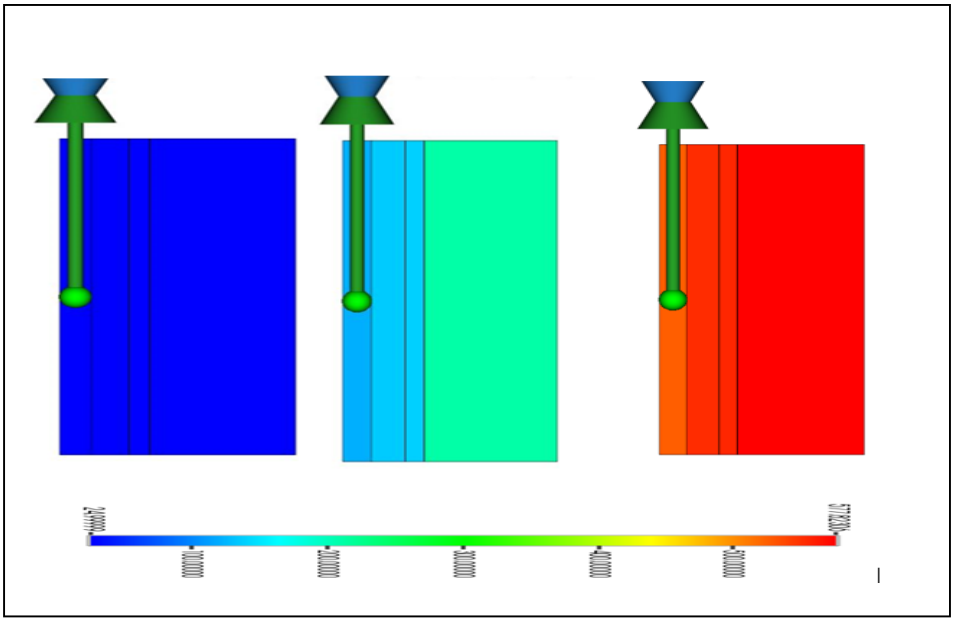

Figure 3.12: Temperature propagation – 0th, 2.30th hour, 5.30th hour (left to right).

Table 3.5: Operational parameters.

Parameter	Value
O2 fraction	0.2073
N2 fraction	0.2079
Operation Pressure	689.5 kpa
Injection Rate	2 l/min
Initial Temperature	25.93 ºC
Heat Transfer Rate	30 J/min

4. RESULTS AND DISCUSSION

After each experiment, the raw data is obtained from the PC connected to the system. The raw data consists of temperature and syngas concentration measurements taken during the experiment.

In the first instance, checking the raw data ensures that the experiment is conducted correctly at the desired heating rate and that any probable mistake or malfunction of the system apparatus can be recognized. Besides, the general behavior trend of the gasification process can be checked for validity.

This section shows temperature, O_2 consumption, and CO_2 production rate data for asphaltite and coal samples. The data will be discussed and compared. Reviewing the production data at laboratory scales provides an idea of the approximate syngas production, which can be used to further implications in by-product optimization, refinery system designs, and plant design operations.

Briefly, each experiment shows two peaks representing LTO (Low-Temprature Oxidation) and HTO (High-Temprature Oxidation) reactions. Also, when the graphs are shown together, a shift is observed, reflecting the different heating rates imposed on the system during the experiment set. Consequently, the conversion is determined for each heating rate.

After obtaining all the sets' conversion and temperature rates, an isoconversational signature is obtained using the isoconversational analysis method. This way, activation energy changes are estimated at the extent of the process. Determining a constant activation energy in each stage of combustion, if possible, provides information on accurate determination of different phases of the process, estimating the similar series of parallel reactions taking place in each phase for asphaltite case, and determining exact reactions for coal sample, getting more resolute idea about the compositions of the sample and the time each group of compositions acts as a reactant and eventually, trying to optimize the kinetic parameters such as enthalpies and frequency factors in kinetic scale. The last point contributes to reaching the optimum and desired syngas production and designing the process in the best way possible for the plants.

4.1 Asphaltite Results

Figure 4.1 shows asphaltite temperature changes during the experiment. Every experiment started at approximately 300 K atmospheric temperature. After a sharp nonlinear increase, at nearly 500 K, the first peak representing LTO reactions is observed. It is followed by a second peak indicating the HTO reactions after a moderate increase. At last, a linear, smooth increase in temperature is observed till the end of the experiment, suggesting that in the process, all the hydrocarbons are converted into end products.

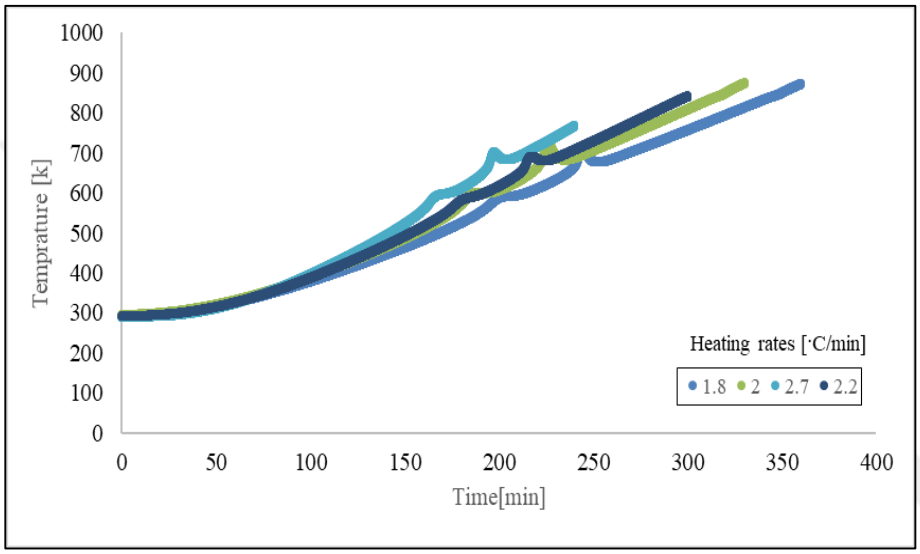

Fig 4.1: Temperature measurements in the reactor for different heating rates – asphaltite experiments.

Figure 4.2 shows oxygen consumption in the experiment through time. It is clear that the highest consumption of oxygen occurs in the 2nd and 4th hour of the experiments when Low-temperature oxidations and high-temperature oxidation reactions occur. From the beginning of the reaction, oxygen is not consumed. Approaching the time of LTO reactions, oxygen consumption starts till during the LTO reactions, 2% of oxygen is consumed, reaching 19% concentration, and then oxygen consumption is fixed at 20% for all of the experiments. Following this, the oxygen consumption increases sharply until the HTO reactions propagate; approximately 4% of the oxygen is consumed in each experiment, and the concentration reaches 16% when HTO reactions occur. Thereafter, the oxygen concentration reaches its initial amount till the termination of the experiment.

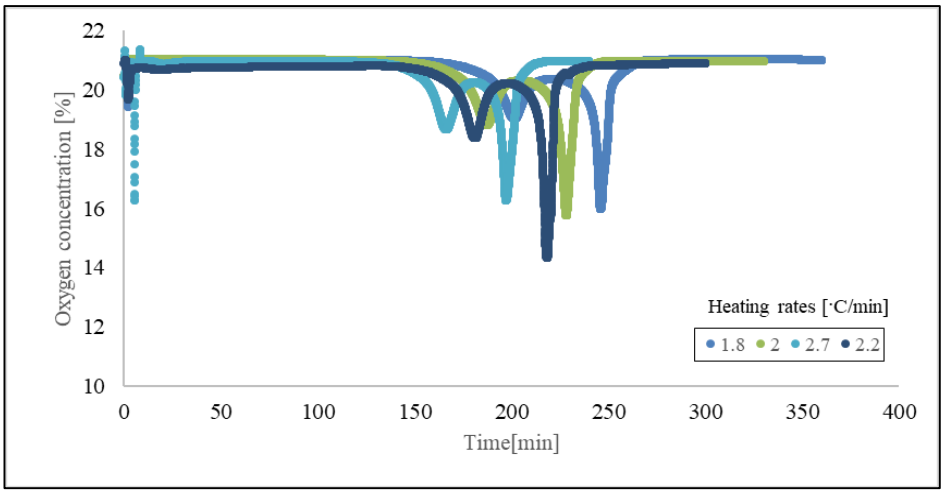

Fig 4.2: Oxygen concentration in the effluent gas – asphaltite experiments.

Figure 4.3 shows carbon dioxide production versus time. Again, as mentioned in the case of oxygen consumption, CO_2 production increases during LTO and HTO reactions. Carbon dioxide concentration was calibrated at zero at the beginning of the experiments. Until the LTO reactions take place, no CO_2 is produced. Near the LTO reactions, at nearly 2nd hour of the experiment, carbon dioxide production starts, and the concentration of CO_2 increases to nearly 1% in the system. After that, it fixes to nearly 0.5% concentration and again starts increasing to 4% when HTO reactions occur. After the HTO reactions, the concentration of carbon dioxide returns to its initial amount of zero.

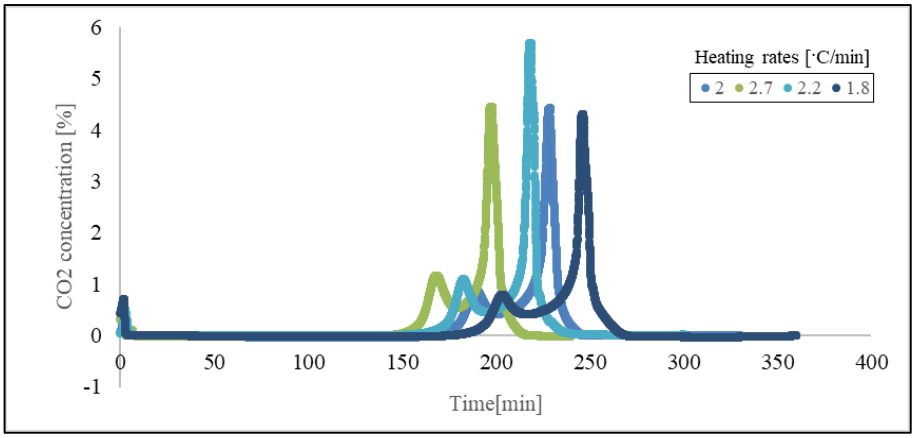

Fig 4.3: Carbon dioxide concentration in the effluent gas – asphaltite experiments.

4.2 Coal Results

Figure 4.4 shows the temperature of the coal sample in the reactor. Experiments start at approximately 300 K atmospheric temperature. After a gradual increase, at nearly 450 K, the first peak is reached, which shows that LTO reactions are taking place in

the system. Consequently, the peak representing HTO reactions is observed in the measurements, followed by the same temperature increase. At last, there is a linear, smooth increase in temperature till the end of the experiment according to the pre-determined temperature program. In coal samples, the first peak showing LTO reactions extends more in time than the HTO part.

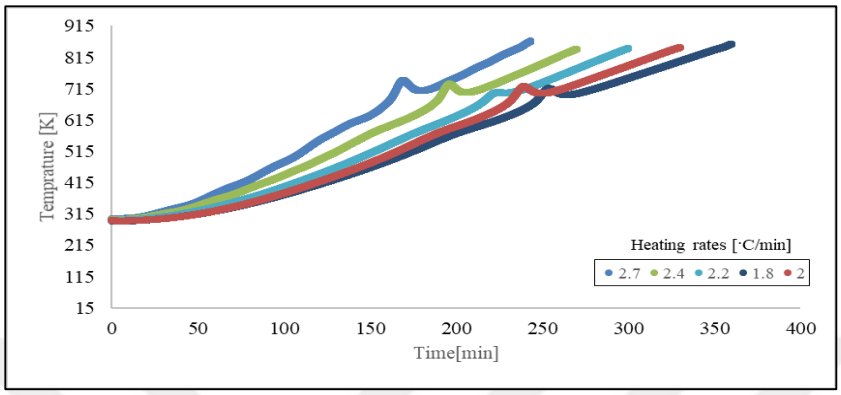

Fig 4.4: Temperature measurements in the reactor for different heating rates – coal experiments.

Figure 4.5 shows oxygen consumption during gasification. Oxygen concentration is calibrated at 21% at the beginning of each experiment. The highest oxygen consumption occurs in the 2nd and 4th hours of the experiments when low-temperature oxidations and high-temperature oxidation reactions occur. At the initial steps of the experiment, oxygen is not consumed. Near the time of LTO reactions, oxygen consumption starts, and during the LTO reactions, 1% of oxygen is consumed, reaching a peak of 20.5% concentration, and then oxygen consumption is fixed at an amount a little less than 20.5%. Following this, the oxygen consumption reaches another peak at HTO. Approximately 2.5% of the oxygen is consumed in each experiment, and the concentration reaches 18%. Thereafter, the oxygen consumption becomes zero until the termination of the experiment.

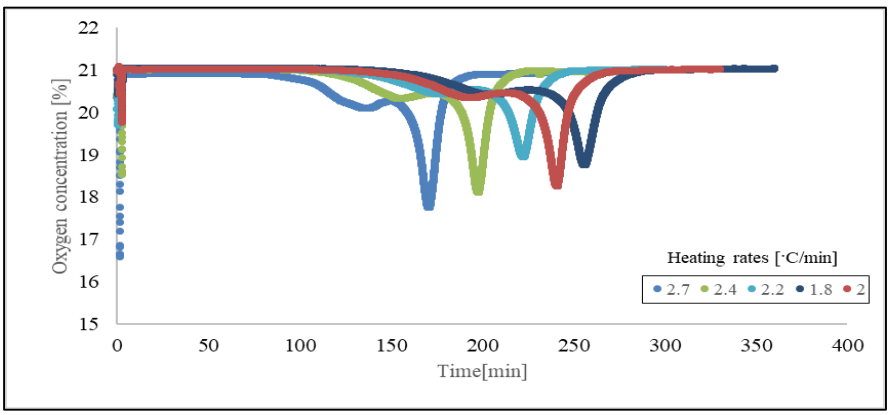

Fig 4.5: Oxygen concentration in the effluent gas–coal experiments.

Figure 4.6 shows carbon dioxide production versus time. Generally, CO_2 production increases in time traversing LTO and HTO reactions. Carbon dioxide concentration is calibrated at zero concentration initially. No CO_2 is produced before LTO reactions. Near the LTO reactions, at nearly 2nd hour of the experiment, carbon dioxide production starts, and the concentration of CO_2 increases to nearly 0.5% in the system. Then, it fixes to an amount very close to 0.5% concentration and then again starts increasing to 2-3% when HTO reactions happen. After the HTO reactions, the concentration of carbon dioxide returns to its initial amount of zero.

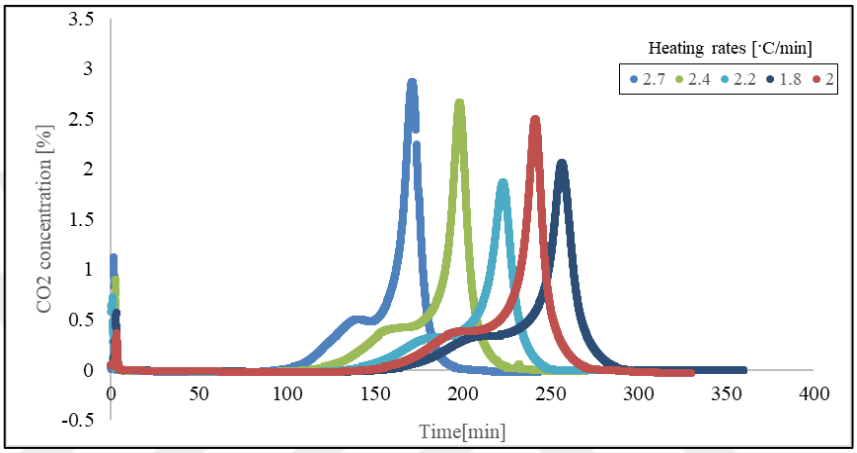

Fig 4.6: Carbon dioxide concentration in the effluent gas–coal experiments.

4.3 O_2 Consumption and CO_2 production

To compare CO_2 production and oxygen consumption in the gasification process, as can be seen in Figure 4.7, the experiments with 2.71 ºC/min are considered. At the first stage, as long as LTO reactions are considered, oxygen consumption is 1 percent more than CO_2 production. However, in the second phase of gasification, when HTO reactions take place, the production and consumption of CO_2 and O_2 are identical, which shows that the oxygen consumed is converted into carbon dioxide.

Generally, oxygen consumption is more than carbon dioxide production in the asphaltite.

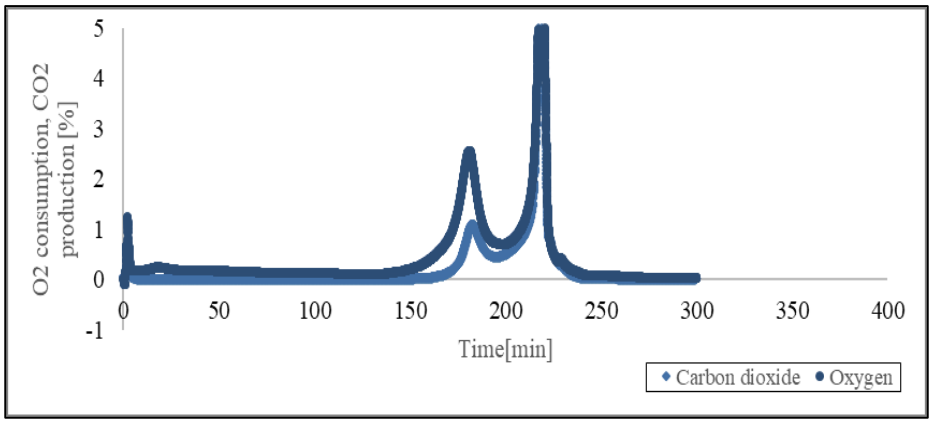

Fig 4.7: Oxygen consumption compared to CO_2 production – asphaltite experiment at 2.20 °C/min.

As Figure 4.8 shows, carbon dioxide production is less than oxygen consumption when LTO reactions occur. However, they are nearly similar in HTO reactions.

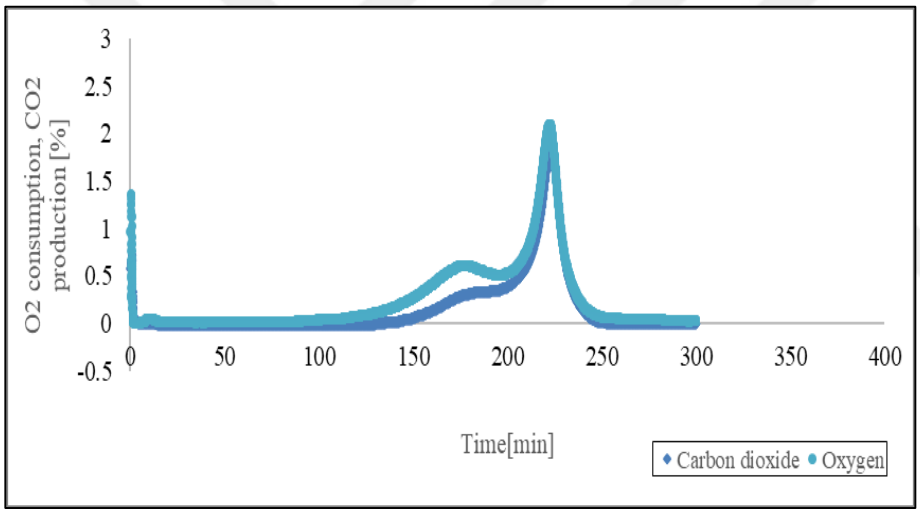

Fig 4.8: Oxygen consumption compared to CO_2 production – coal experiment at 2.20 °C/min.

4.4 Discussion

Figures 4.9, 4.10, and 4.11 show temperature, oxygen consumption, and CO_2 production rates for both asphaltite and coal samples.

Firstly, while crude oil, as studied by Cinar (2011) and asphaltite samples, seems to start LTO reactions at 500 K, in the case of coal, this happens at 450 K. This can indicate that in this set of experiments, the applied coal sample contains more volatile matter than asphaltite. This can also be approved in the further analysis section. On the other hand, in the HTO region, coal seems to start reacting later than asphaltite.

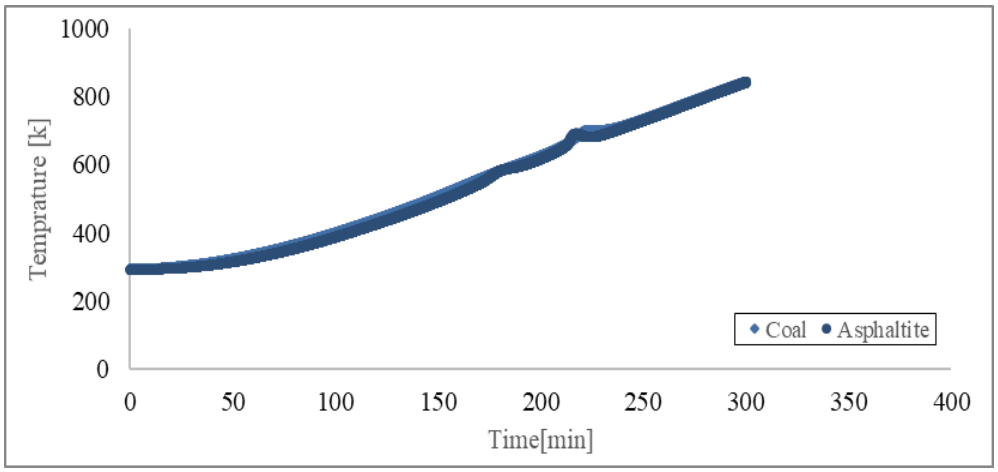

Fig 4.9: Reactor temperature measurements compared for the heating rate of 2.2 ºC/min.

Carbon dioxide production in the asphaltite case is around twice that of the coal sample. This indicates that the reactions that lead to CO_2 production play a more important role in this case. Asphaltite has more sulfur, magnesium, and calcium than coal. Also, as a side product of hydrogen reactions, it can be concluded that methane may be converted to CO_2 in these series of multi-step reactions.

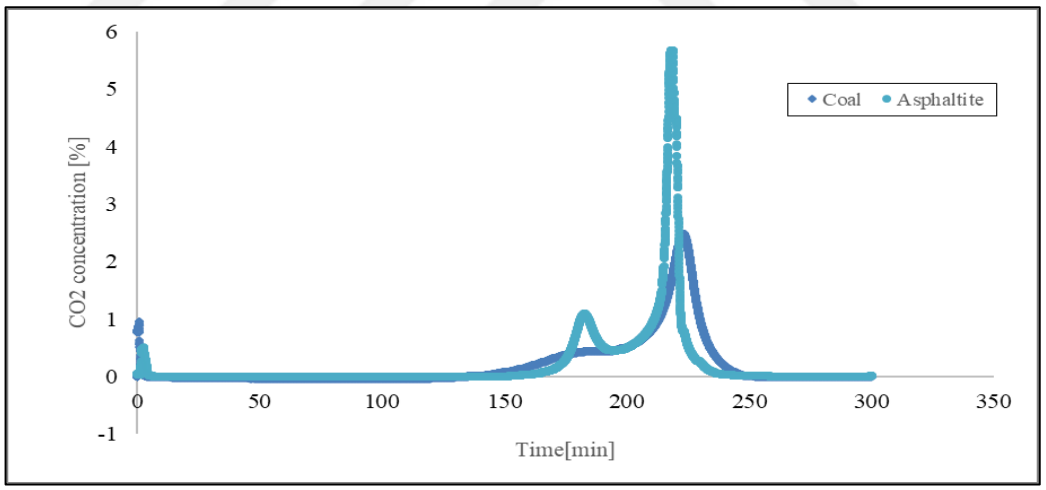

Fig 4.10: CO_2 production compared for heating rate of 2.2 ºC/min.

As mentioned before, oxygen is consumed more in the case of asphaltite. This difference is more significant in the LTO phase. It can be concluded that oxygen is more involved in reactions in the asphaltite sample, and therefore, the reaction series is more complex and probably more numerous compared to coal.

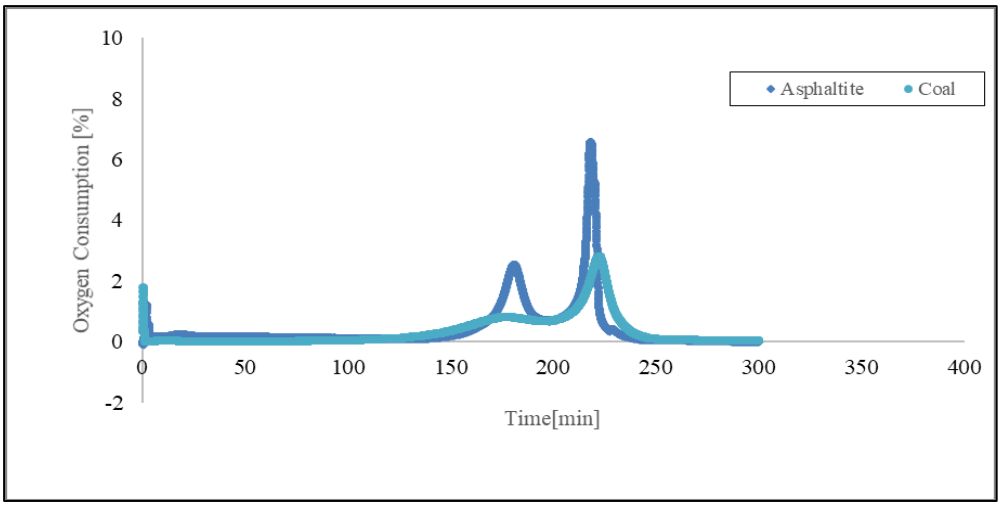

Fig 4.11: O_2 consumption compared for heating rate of 2.2 ºC/min.

4.5 Kinetic Analysis

As mentioned above, coal and asphaltite seem to be involved in a series of parallel, multi-step reactions in the gasification procedure—the complicated and heavy molecule structures in both samples mainly cause this. As a result, it would not be easy to have a fixed chemical reaction model predicting the steps of gasification in a clarified way. To overcome this, kinetic analysis is so far the best technique suggested that can be used to represent approximately the specific stages involved in the gasification process of each sample and, at the same time, allow the prediction of this procedure at any time, temperature, and amount of different samples.

Kinetic analysis can be defined as the various techniques that can be utilized to determine the rate laws of the reactions, which helps with having an idea about the overall reaction mechanism and scheme (Chemistry Department of the University of Arizona, n.d). The very general kinetic equation assumes the reaction rate is dependent on temperature and concentration and can be represented as follows in Equation 4.1.

$$r=K(T)f(C) \quad \textbf{(4.1)}$$

The first term, K(T), is called the reaction rate constant and is, in most cases, a strong function of temperature. Considering an elementary treatment, Arrhenius proposed an equation in 1889 relating activation energy and temperature to the reaction rate, given as Equation 4.2.

$$k\,(T) = Ae^{-E/RT} \quad \textbf{(4.2)}$$

where E is the activation energy, R is the gas constant, T is the temperature, and A, the constant of proportionality, is the pre-exponential factor or frequency factor that defines the frequency at which reactant molecules are colliding and the probability of a successful reaction at a specific temperature.

The second term, meanwhile, shows the dependency of the reaction rate on concentration, in which the order of the reaction may be of importance. This can be determined considering the experiment and is usually presented by power laws in the simplest way. While it might seem easy to determine this value in elementary reactions, in multi-step reactions, it is complicated since the data obtained from the experiment, the reaction mechanisms, and, in some cases, intermediate fractions involved in experiments might need to be clarified or easier to define.

In fact, Arrhenius theory intends to behave with reactions, regardless of being single or complex, as a complement reaction while primarily obtaining this fit in experimental data might be challenging. Taking Arrhenius theory and mathematical derivations into consideration, linear as studied by Bousaid and Ramey (1968), or non-linear regression as studied by Abukhamsin et al. (1988) is applied to the equation; in this way, activation energy is obtained.

Generalizing this theory for this study requires different corrections and assuming particular conditions, such as isothermal conditions and unity order, which seems to be hard to reach in this set of experiments (Bousaid and Ramey, 1968). Several modifications and improvements have been made based on Arrhenius's theory, namely Fassihi (1981); however, as mentioned before, each and every one of them is valid in particular conditions.

To overcome the inconsistencies that originated from using Arrhenius's theory, the isoconversational or so-called Friedman method investigated by Friedman (1964) comes up. This method assumes that the reaction rate at a constant extent of conversion is only a function of temperature (Simon, n.d). In its most general way, Equation 4.3 is taken into consideration studied by Friedman (1984) and Cinar (2011):

$$dx/dt = Ae^{-E/RT} f(x) \quad \textbf{(4.3)}$$

In this case, x is the conversion, t is time in terms of hours, T is the temperature in K, and R is the gas constant considered 1.987 cal/kmole. Taking ln from both sides yields equation 4.4.

$$\ln(dX/dt) = \ln(A) + \ln[f(X)] - E/RT \quad \textbf{(4.4)}$$

Assuming the above presumptions, the equation can be rewritten as equation 4.5.

$$\ln (dX/ dt)= m – 1/ R * E/T \quad \textbf{(4.5)}$$

Therefore, plotting the LHS of this equation with respect to the RHS of it easily yields the activation energy as a slope. As shown step by step, this method provides an opportunity to comprehend the reaction mechanism and scheme in a different way. However, the resulting activation energies are effective rather than specific because the dominant reaction changes at the extent of conversion, the activation energy. Throughout the transition, effective values are observed in the isoconversional plots. Thus, the graphs give the evolution of reactions at the extent of conversion. That's the reason for the negative values obtained. Furthermore, as an important advantage, this method makes it possible to reach this goal with the most in-hand data directly obtained from the experiments, namely temperature, conversion, and time. Obtaining the activation energy not only helps with the mentioned points above but also is a favorable guide in developing chemical processes and optimizing reaction conditions and apparatus on both industrial and laboratory scales.

To meet this end, a set of experiments with different heating rates must be conducted. To ensure consistency, which is an essential factor in the isoconversational analysis stated by Cinar (2011), all other factors, namely pressure, flow rate, and starting temperature, are the same for all sets of experiments. Once conducted, raw data, consisting of effluent gas concentrations and temperature at each time, is obtained for each heating rate, as mentioned beforehand. By applying mathematical interpolation, integration, numerical differentiation, and summation methods to the raw data investigated by Cinar (2011), conversion is calculated at each temperature.

4.5.1 O_2 consumption analysis

Figure 4.12 and Figure 4.13 show conversion versus time for asphaltite and coal samples, respectively. It is clear that different heating rates lead to the shift observed in the graphs. Besides, coal shows more clarified behavior than asphaltite in a way that, although asphaltite graphs show the shift, the data may overlap in some parts. Considering that this graph is based on mathematical calculations, the data obtained from the experiment may cause some errors, probably coming from complex mechanisms, reactions, and sample structure. Generally, looking at the graph, it is recognized that the overlaps and mixed behaviors take place in the first phase of the combustion process of lighter or immediate components of the sample, in other words.

Mathematical calculations also, as mentioned, need some corrections and contain some errors, so these errors from both calculation and data might reflect themselves on the plot. Besides, as reflected in the graph, a dramatic increase in conversion is observed starting from the LTO (low-temperature oxidation) and continuing to HTO (high-temperature oxidation), approximately between 600 to 700 K, for both samples. Interestingly, both asphaltite and coal samples show the mentioned increase in two steps, reflecting the LTO and HTO at about 0.2 and 0.8 conversions, respectively. In the case of asphaltite, this two-step increase is sharper than coal, which can be explained by heavier intermediate structures and reaction mechanisms of asphaltites, which are described in other parts.

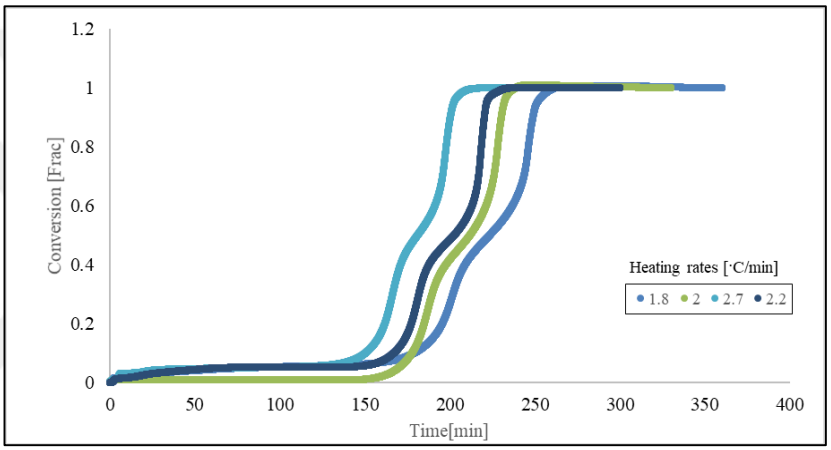

Fig 4.12: Conversion based on O_2 consumption- asphaltite.

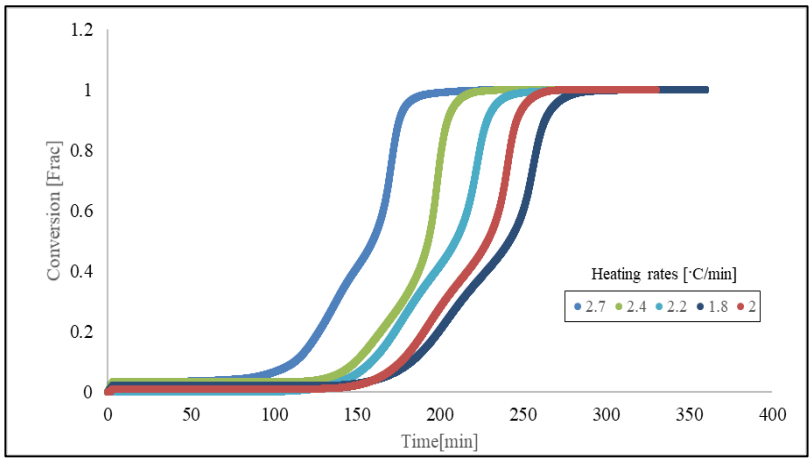

Fig 4.13: Conversion based on O_2 consumption - coal.

In the next step, specific selected conversions at each heating rate should be considered, and linear regression must be performed on the data, resulting in activation

energy. Introducing the data into a programming language, MATLAB, linear regression is performed, and eventually, the graph of activation energy with respect to conversion is obtained for each set of experiments on asphaltite and coal samples, as seen in Figure 4.14 and Figure 4.15, respectively.

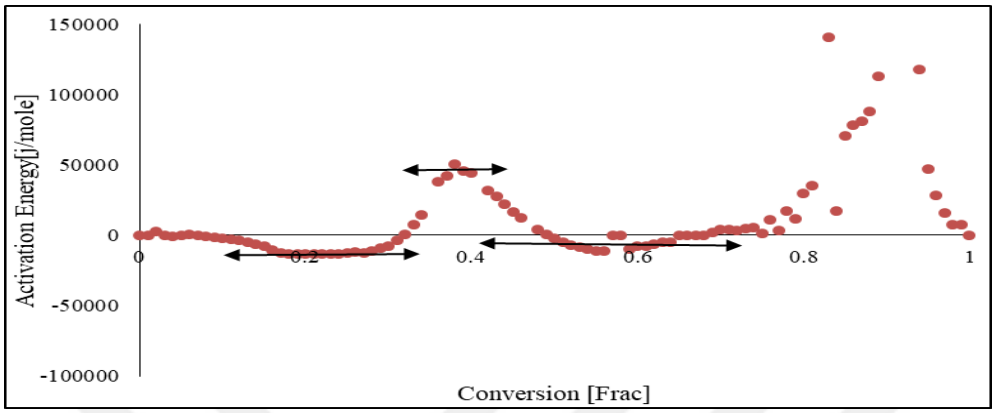

Fig 4.14: Isoconversional fingerprint based on O_2 consumption – asphaltite.

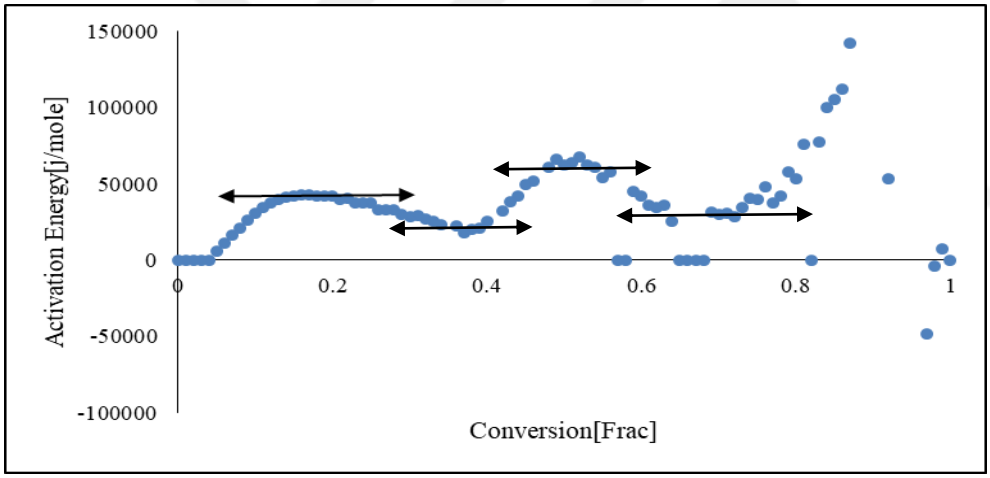

Fig 4.15: Isoconversional fingerprint based on O_2 consumption – coal.

While coal's activation energy varies between 0 to 150 kJ, asphaltite's is shown to differ similarly. In the coal sample, the conversion shows a moderate increase, continuing to a 0.15 conversion, probably due to the presence of volatile matter in coal (Cakal et al., 2007; Verma et al., 2020). Starting from 0.15 conversion till 0.4, a down peak of 20 kJ/mole activation energy is reached. The second peak reached about 0.55 conversion with an activation energy of 60 kJ /mole. Then, the third peak reached about 0.8 conversion of about 30 kJ/mole. Eventually, the last peak is observed at the end of the experiment due to the least remaining particles and, therefore, the highest energy needed to finish the combustion process at high temperatures, showing 140 kJ

/mole. Two prominent peaks and activation energies are involved in this mechanism, reflecting the LTO and HTO, respectively.

Further, reviewing the literature from Cinar (2011) and Verma et al. (2020) shows that the coal sample indicates almost the same trends and peaks as crude oil except for a slight upward shift in the graph. This may be due to the high existence of volatile matter, which leads to higher reactivity (Cakal et al., 2007; Fermoso et al., 2009; Verma et al., 2020). This, alongside the existence of elements like calcium, magnesium, potassium, and sodium, may be the reason for the difference between the two graphs in the first phases of the gasification (Glatz, 2011; Jayaraman and Gokalp, 2015; Nemanova, 2014). The other difference noteworthy to be mentioned is that between 0.4 and 0.8 conversions, while crude oil tends to show an increase or slight increase in some phases, the coal sample's activation energy shows a decrease, followed by an increase after 0.7 conversions. This may be interpreted as if the intermediate mechanism concerning the gasification process requires less energy due to lighter components in the intermediate reactions in coals than in crude oil and higher energy rates in the last conversions due to heavier and ash components in the coal sample. Also, as in crude oil samples studied by Cinar (2011), the two peaks in the graph represent the temperature at which LTO and HTO occurred, respectively, at about 0.4 and 0.8 conversions.

In the case of asphaltite, however, analyzing the result is more challenging than it seems. The asphaltite sample shows very complex behavior, making it hard to analyze the results. Generally speaking, the range of activation energy variation in asphaltite is higher than in crude oil and coal samples, which is predictably due to the tar, benzene, sulfur, and ash components of asphaltites. Starting from a 0.1 conversion, the activation energy decreases to approximately -25 kJ/mole and remains constant until a 0.3 conversion. This phase mostly deals with volatile matter and moisture contents (Tonbul et al., 2009). Thereafter, a dramatic rise to 100 kJ/mole followed by a dramatic drop to the previous value occurs between 0.3 to nearly 0.6 conversion. This region is where complicated reactions such as tar formation or simulations parallel reactions happen, making it hard to recognize (Tonbul et al., 2009; Aksogan Korkmaz and Ozbas, 2017). Eventually, an increase can be observed from 0.6 conversion until the end of the experiment. Considering all points, four peaks are noticed in asphaltite sample gasification, just as they were in coal.

As mentioned before, determining an average activation energy can significantly contribute to different fields. As long as asphaltite is considered, it is more complicated since the energy levels fluctuate significantly. Yet, as shown in Figure 4.13, three average activation energies of -12.7, 45, and -2 kJ/mole are determined for the first phases, LTO and HTO stages. As long as coal is taken, four activation energies for different stages are defined as 40, 24, 60, and 30 kJ/mole for the first, intermediate, LTO, and HTO stages.

As observed in Figure 4.16 and Figure 4.17, which is studied by Cinar (2011), that shows the coal, asphaltite, and crude oil activation energy changes with conversion; in the first conversion reaching 0.25, the asphaltite sample behaves similarly to crude oil, both in terms of range and trend. Nevertheless, the upcoming behavior, between a conversion of 0.4 and 0.7, shows no exact similarity with coal or crude oil. However, crude oil and asphaltite show some similarities to the conversion of 0.4 to 0.5, which is the region of LTO reactions. The behavior of coal samples in this range of conversion is reported to be due to the high carbon content of coals (Cakal et al., 2007; Glatz, 2011). This high carbon content leads to complicated, multi-step reactions in the gasification procedure, eventually resulting in high activation energy changes in the mentioned range (Cakal et al., 2007; Verma et al., 2020). Therefore, one can conclude that the carbon contents of asphaltite used in this set of experiments are lower than the coal sample (Verma et al., 2020). Still, after 0.7 conversions, in the last phases of converting, asphaltites show a similar increase to that in the coal sample, which likely explains why the heavier components are almost from the same group. One possible explanation questions the applicability of the isoconversional principle on asphaltite gasification. The isoconversional principle could not hold for this particular hydrocarbons. Further studies are needed to clarify.

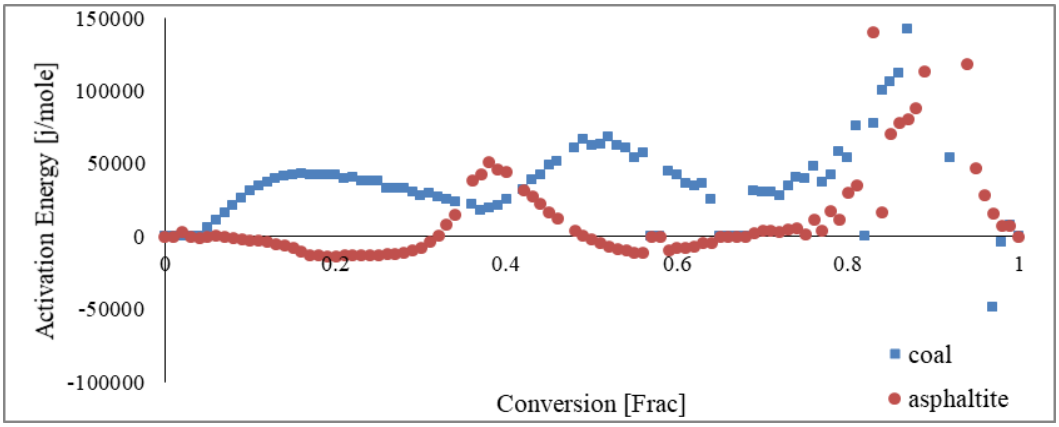

Fig 4.16: Isoconversional fingerprint based on O_2 consumption compared.

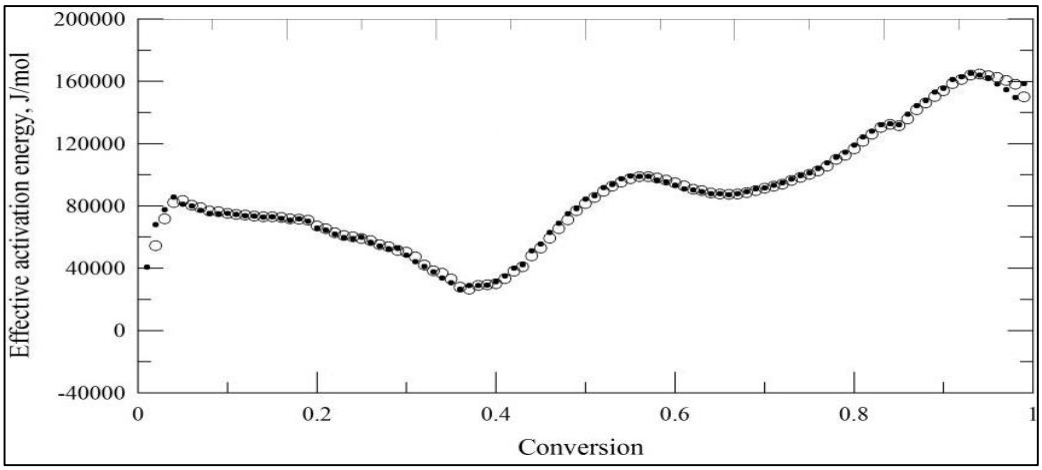

Fig 4.17: Isoconversional fingerprint for crude oil (Cinar, 2011).

It can be concluded that, in the first conversions, mechanisms and components may be more similar to crude oil, while the last ones show more similarity to coal samples. Noting that, when it comes to intermediate reactions, there can not be any certain saying either due to complex structure containing ashes and impurities or non-definable multi-step, simultaneous, parallel reactions involved in the asphaltites gasification process in intermediate procedures (Tonbul et al., 2009). Again, in the case of asphaltites, peaks mirroring LTO and HTO are observed at about 0.4 and 0.8 conversions as in coal and crude oil samples at almost the same temperatures but in totally different values of 100 and -25 kJ/mole, respectively. Furthermore, it can be concluded that the two main activation energy estimations and peaks in the asphaltite case are also based on LTO and HTO in the same manner as previous cases.

The analysis above was done using the oxygen consumption data. In the following steps, to better understand the behaviors coal and asphaltite show and to consider all the reactions that might take place and affect the plots' trends, other effluent gas compositions, namely CO and CO_2, are analyzed.

4.5.2 CO production analysis

Carbon monoxide is not generally analyzed since its measurements almost always involve noise and errors. As can be seen in Figure 4.18 and Figure 4.19, carbon monoxide conversion is plotted versus time for asphaltite and coal samples, respectively.

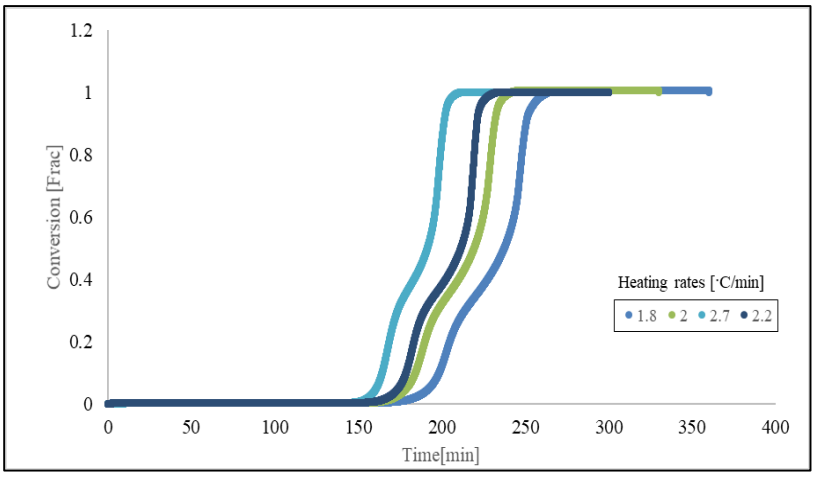

Fig 4.18: Conversion based on CO production – asphaltite.

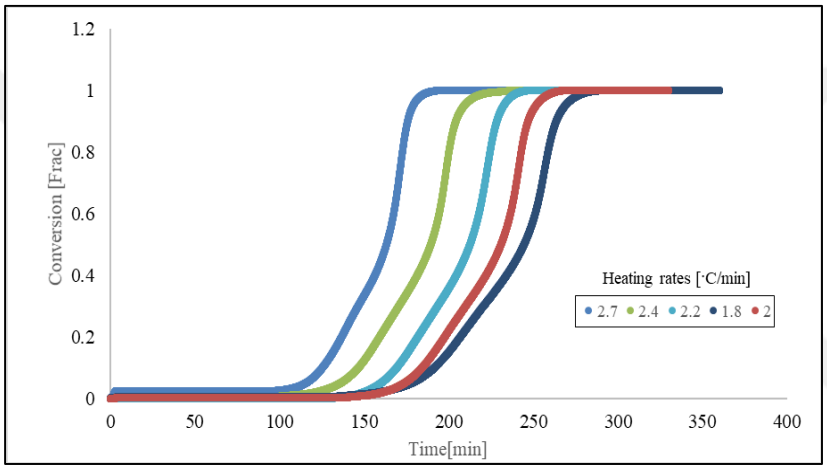

Fig 4.19: Conversion based on CO production – coal.

There again, the shifts in the graph show different heating rates for this set of experiments. Furthermore, approximately near the lower temperature oxidation, which is represented as about 0.4 conversions, the significant rise in conversion starts and continues till the end of the gasification procedure for both of the samples around the temperature 600-700 K. Besides, the conversion shows non-linear behavior reaching the time of high-temperature oxidation. This behavior is more remarkable in asphaltite. All the points mentioned above related to the conversion plot are valid in this part.

In the conversion versus activation energy plots, in the case of asphaltite, as observed in Figure 4.20, the activation energy changes in the range of -45 kJ /mole and 30 kJ/mole. Obviously, since ashes are reacting at the end of the gasification process, higher activation energies in the range of 210 kJ/mole are observed. Once again, there are two peaks visible in the phase of LTO and HTO reactions in the asphaltite graph between 0.4 and 0.8 conversions, showing 30 and 20 kJ/mole, respectively.

Taking the coal graph into consideration, as shown in Figure 4.21, the variation of activation energy is approximately half that of asphaltite and only positively. Again, two peaks of LTO and HTO reactions are noticeable at 10 and 17 kJ/mole, respectively.

All in all, from Figure 4.22, it can be understood that CO is not or slightly produced in asphaltites during the LTO phase reactions. However, the opposite is noticeable in coal LTO phase reactions. Furthermore, again, asphaltite and coal are approved to behave approximately the same in HTO; it can be concluded that CO-producing reactions and mechanisms play an important role in this phase.

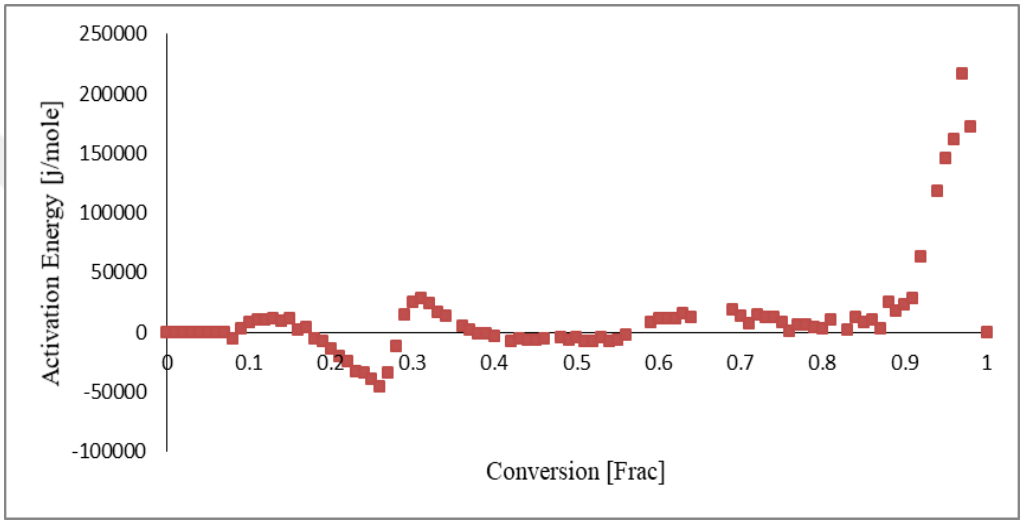

Fig 4.20: Isoconversional fingerprint based on CO production - asphaltite.

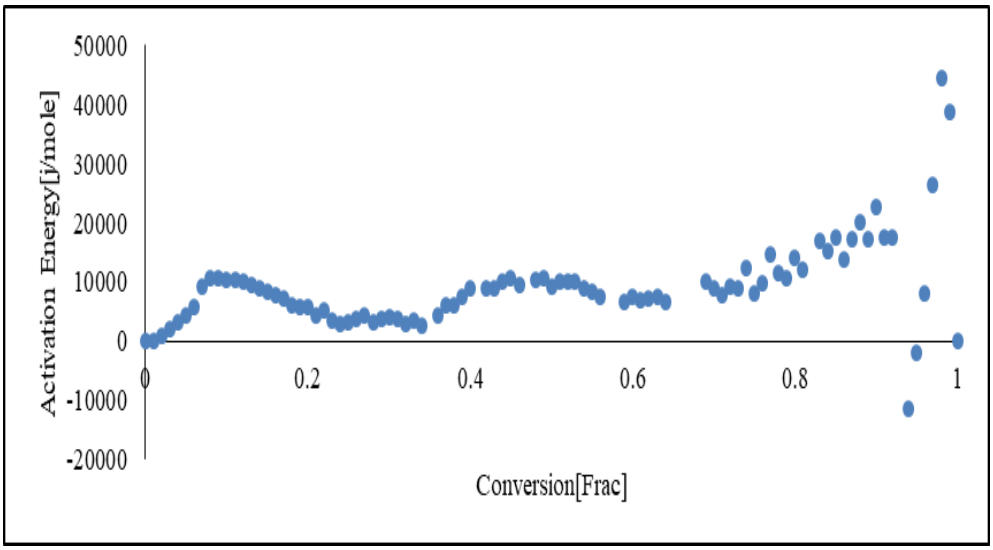

Fig 4.21: Isoconversional fingerprint based on CO production - coal.

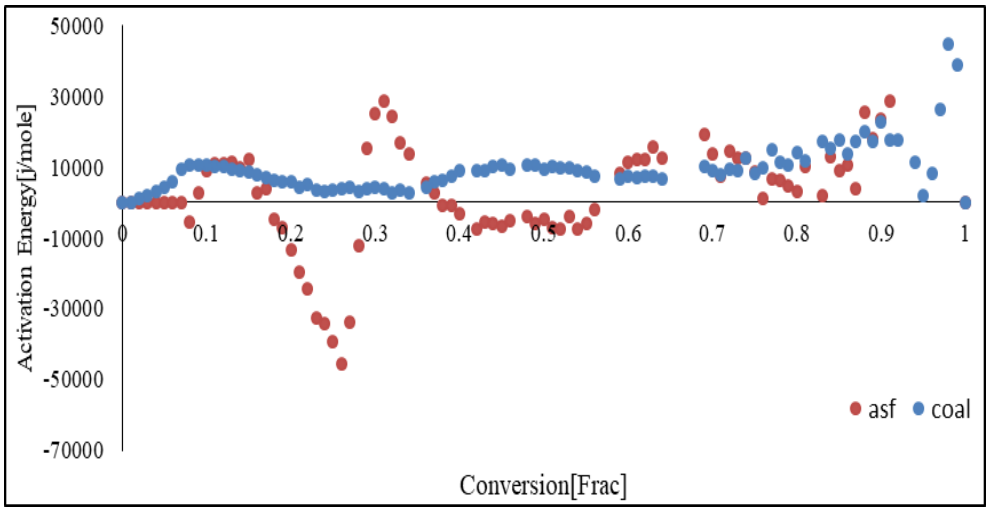

Fig 4.22: Isoconversiona fingerprints compared for asphaltite and coal-based on CO production.

4.5.3 CO_2 production data analysis

In this step, carbon dioxide production data is taken for analysis in each set of experiments. As shown in Figure 4.23 and Figure 4.24, which shows conversion versus time for asphaltite and coal, shifts represent the different heating rates applied in each conducted experiment. Thereafter, as seen in other analyses, Asphaltite data shows a step increase, while coal data tends to behave more smoothly. This can also lead to errors in analysis because, as mentioned before, the isoconversional method presumes only dependence on temperature at the same extent of conversion (Simon, n.d). Again, all of the comments made on the other part are valid in this part.

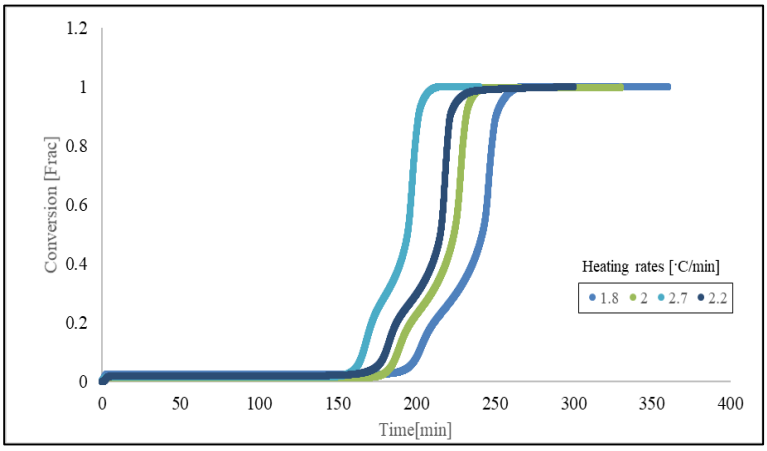

Fig 4.23: Conversion based on CO_2 production – asphaltite.

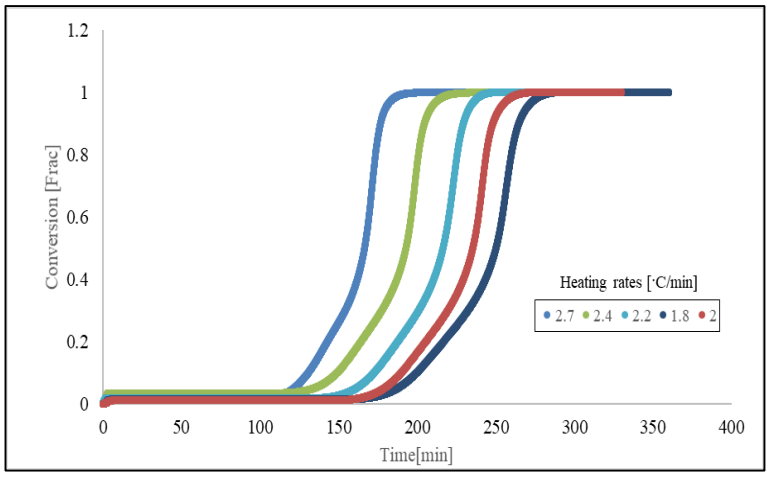

Fig 4.24: Conversion based on CO_2 production – coal.

When it comes to activation energy plots, as can be seen in Figure 4.25, the asphaltite activation energy range varies between -30kJ and +30kJ. First, there is an increase in activation energy to 0.15 conversion, which is the section related to volatile and moisture content. Then, followed by a decrease to 0.35 and staying constant, a moderate increase occurs until the combustion process ends.

Taking the coal sample activation energy variation into consideration, shown in Figure 4.26, after an increase until 0.15, the activation energy drops gradually until 0.5 conversion, and again, it slightly increases until the end of the process. The activation energy shows variation between 5 kJ/mole and 40 kJ/mole in coal.

Compared to oxygen data, carbon dioxide shows more consistent results in determining average activation energies. For asphaltite, -10, 3.6, and coal, 14, 5, and 12 kJ/mole are determined for the pyrolysis and gasification stages, which consist mainly of LTO and HTO reactions.

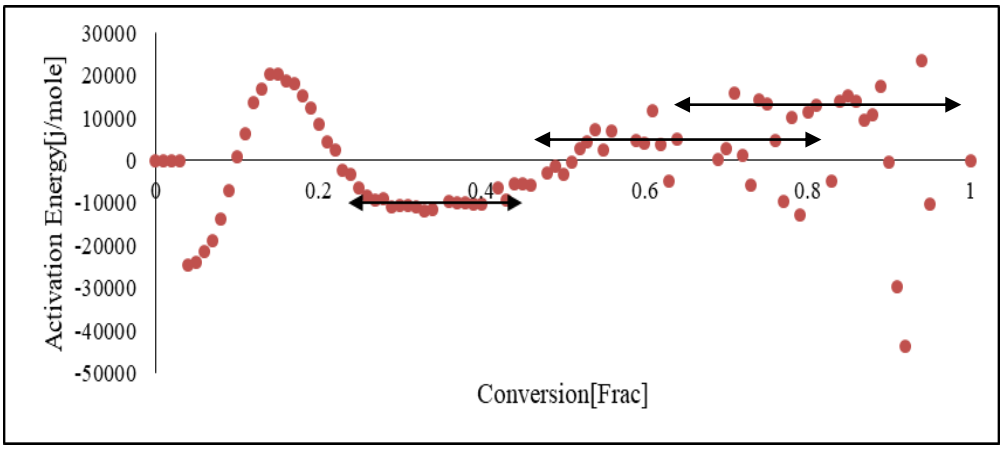

Fig 4.25: Isoconversonal fingerprint based on CO_2 production - asphaltite.

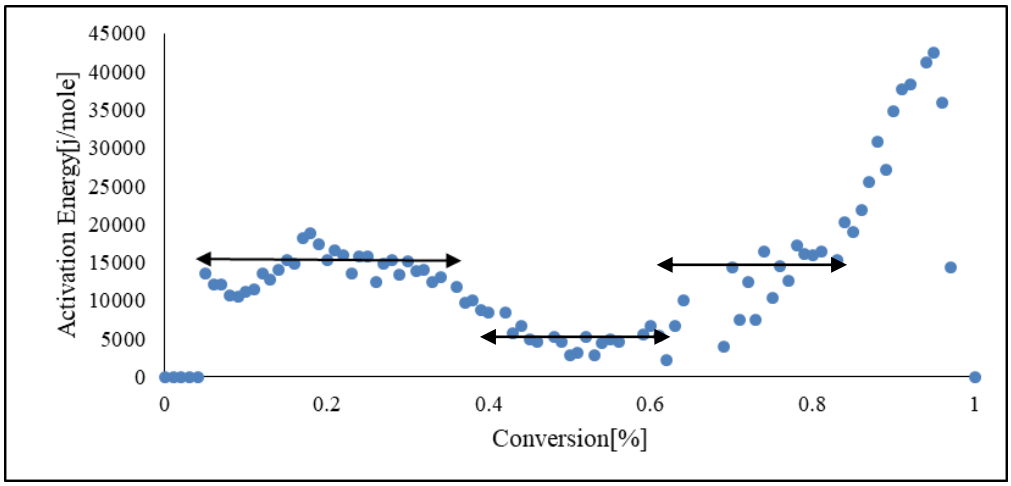

Fig 4.26: Isoconversional fingerprint based on CO_2 production – coal.

As observed in Figure 4.27, if we want to compare coal and asphaltite sample activation energy variation trends using carbon dioxide production data, they show almost the same behavior. The coal sample shows moderate shifts, while asphaltite, on the other hand, shows the same shifts but sharper up to almost the middle of the LTO. After that, both of the samples show the same behavior of increasing. Therefore, to conclude, CO_2 production reactions and mechanisms are probably the same in both samples. These reactions are mostly the ones in which carbon content directly reacts; as a result, supposedly, the carbon contents of intermediate reactants in both asphaltite and coal samples seem to be similar.

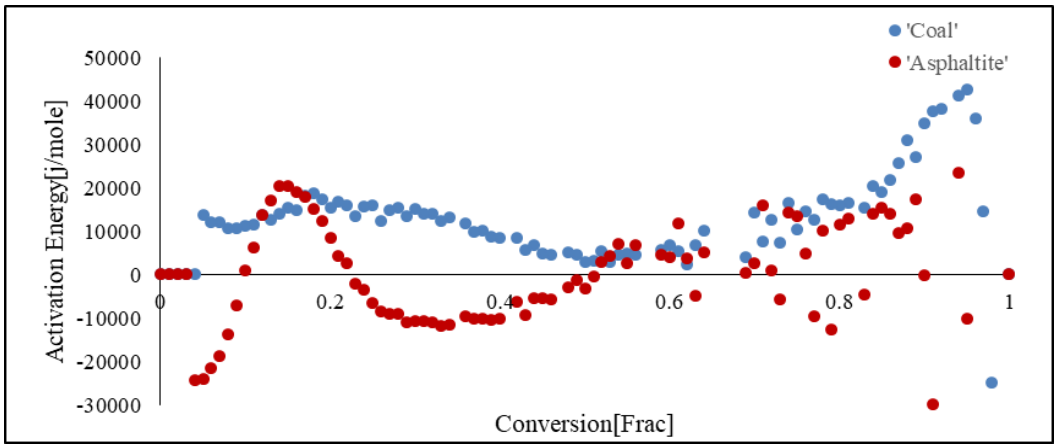

Fig 4.27: Isoconversional fingerprint compared based on CO_2 production.

4.5.4 CO_2 Production, O_2 Consumption Analysis

Figure 4.28 compares CO_2 production and O_2 consumption activation energies regarding conversion for the asphaltite sample. In the first phases of combustion, it can be observed that reactions, including oxygen as a reactant, are not the only reactions

leading to carbon oxides. Nevertheless, after a 0.5 conversion, representing the HTO region, oxygen controlled the reactions involving CO_2 production nearly until the end of oxidation. Generally, it can be concluded that in the first phase of combustion, after the volatile matter reactions, reactions leading to the production of carbon oxides and consumption of oxygen are the same. As in the LTO phase, oxidation reactions are not involved with carbon dioxide production; it is important to mention that in this region, lighter components are involved in reactions. Later on, in the HTO region, as heavier components are reacting, most of the reactions probably involve more carbon oxidations, and thus, more CO_2 is produced.

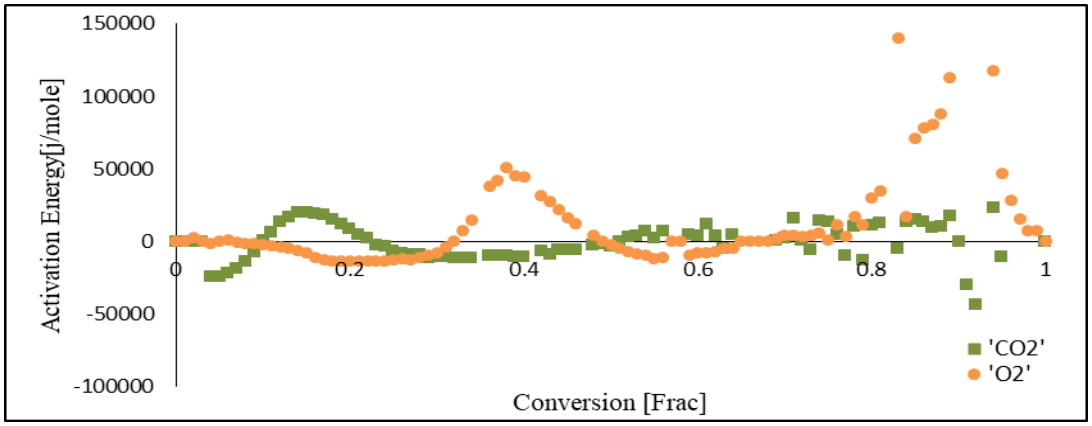

Fig 4.28: Isoconversional fingerprints compared based on oxygen and carbon dioxide- asphaltite.

In the case of coal, as demonstrated in Figure 4.29, the trend is almost the same, which suggests that oxygen is controlling reactions leading to CO_2 production or considering carbon dioxide as a reactant in all of the phases of gasification. The general higher activation energy is an indication of this point.

Generally speaking, as long as volatile matters of coals are involved in reactions, the activation energies are almost the same, which means nearly one mole of oxygen reacted may lead to one mole of carbon dioxide production. In the LTO regio, until 0.6 conversion, the opposite is valid, and oxygen has the main control in the reactions. Approaching the HTO region, the same stoichiometry reactions can be concluded.

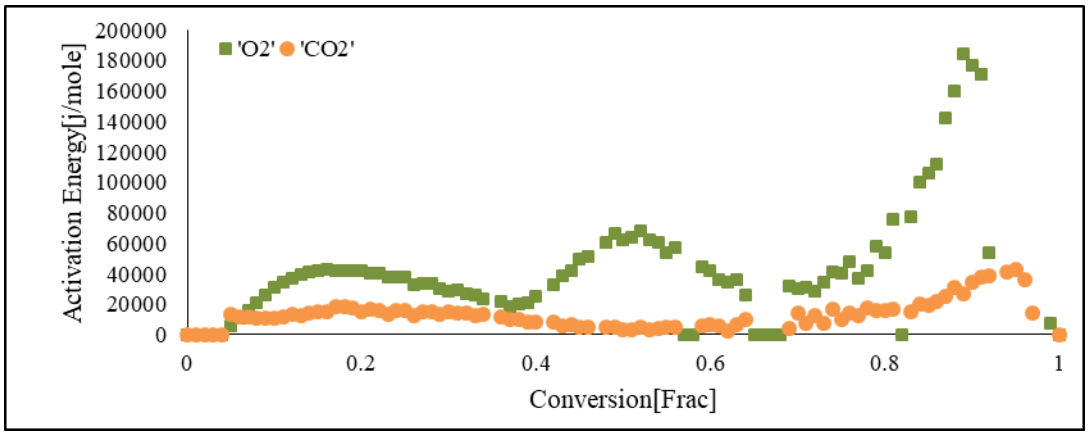

Fig 4.29: Isoconversional fingerprints compared based on oxygen and carbon dioxide - coal.

4.6 CMG Results and Discussions

In this stage, temperature and oxygen consumption rates are obtained. This section considers the data obtained for the experiment with a heating rate of 2 ºC/min as an example.

As displayed in Figure 4.30, the temperature versus time is graphed. Again, the two peaks show the HTO and LTO reactions. The LTO occurs approximately in the third hour, and the HTO occurs in the fourth hour.

The next graph obtained from the simulation is the oxygen consumption rate. Repeatedly, the two peaks demonstrate low-temperature and high-temperature oxidation, as shown in Figure 4.31.

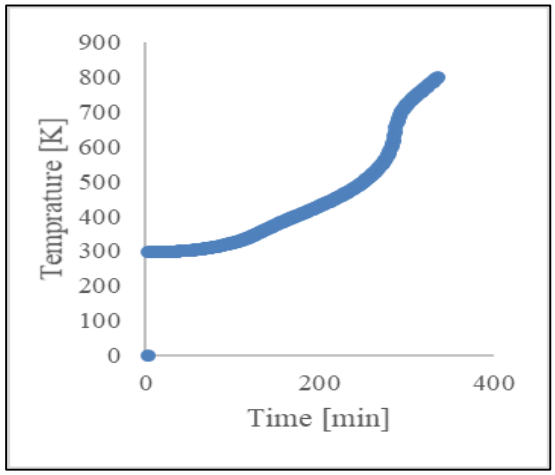

Figure 4.30: Temperature rate for heating rate of 2 ºC/min.

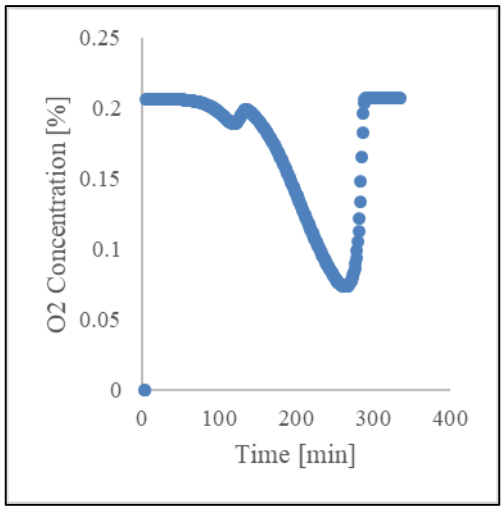

Figure 4.31: Conversion for heating rate of 2 ºC/min.

As can be seen in Figure 4.32, Comparing temperature rates for simulation and experimental results, both graphs show almost the same behavior except for the time intervals the HTO and LTO reactions take place, which can be due to the kinetic parameters and probable differences in the conditions. The target here is not to get a perfect match. Therefore, the results are validated.

On the other hand, comparing conversions obtained from simulation to experimental results, as seen in Figure 4.33, as expected, the behavior of both of them are compatible. It is worth mentioning that the simulation results are broadened in the HTO phase compared to the experimental results, which is potentially due to parameters like enthalpy. Additionally, the absolute error of oxygen conversion is reported as 3 %. Error is higher in oxygen consumption data, which is a result of the simplicity suppositions and potential incompatibility of some inputs with the real-world data, considering that the ideal match is not aimed in this modeling.

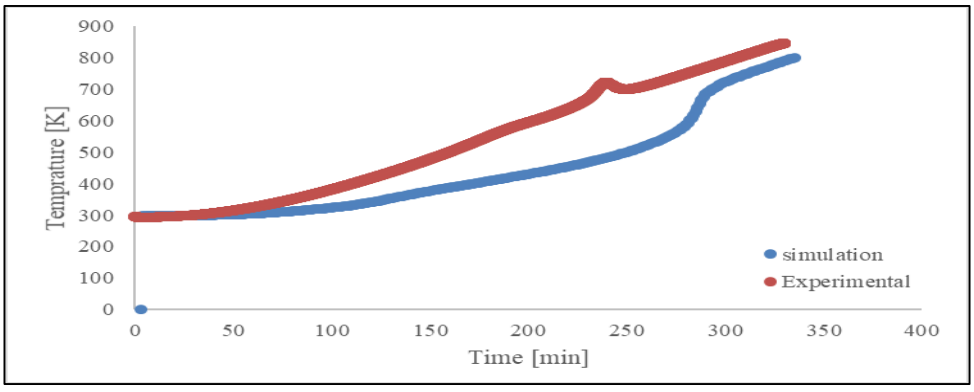

Figure 4.32: Temperature rates compared for heating rate of 2 ºC/min.

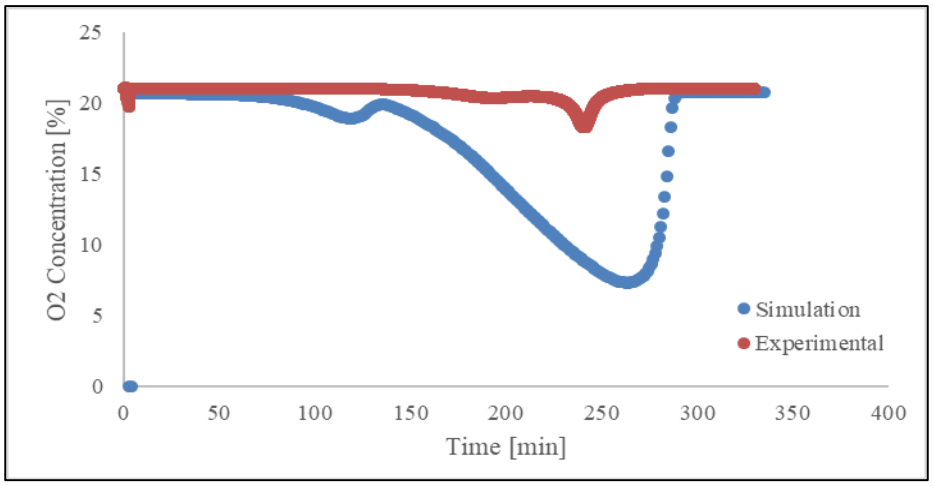

Figure 4.33: Conversion compared for heating rate of 2 ºC/min.

Oxygen consumption and temperature rate for all the heating rates used in this simulation are shown in Figure 4.34 and Figure 4.35. As seen in Figure 4.36, oxygen consumption increases with the increase in heating rate. Thus, a shift is observed in the figure. This means that oxygen consumption starts earlier in higher heating rates, and therefore, it is concluded that the reactions start happening earlier in higher temperatures, as validated in Figure 4.35. The two peaks in the graph show the phases in which LTO and HTO reactions take place, respectively. HTO reactions need more oxygen, as reflected in Figure 4.34. In the simulation, contrary to the experiments, the start of the HTO phase is not sharp after the LTO reactions, which may be due to the differences in parameters like enthalpy.

After simulating the gasification process with all the same heating rates as in the experimental set, isoconversional methods are used to analyze the results and to obtain activation energy variations in different conversions. Neglecting the scales, since the conditions and structure are not one-to-one the same and the purpose is not to get an ideal match, it can be observed that both of the graphs show the same trend as seen in Figure 4.36. In the HTO and LTO phases, which are the most important phases for analysis, it can be seen that both are compatible with each other and therefore, the results obtained are validated.

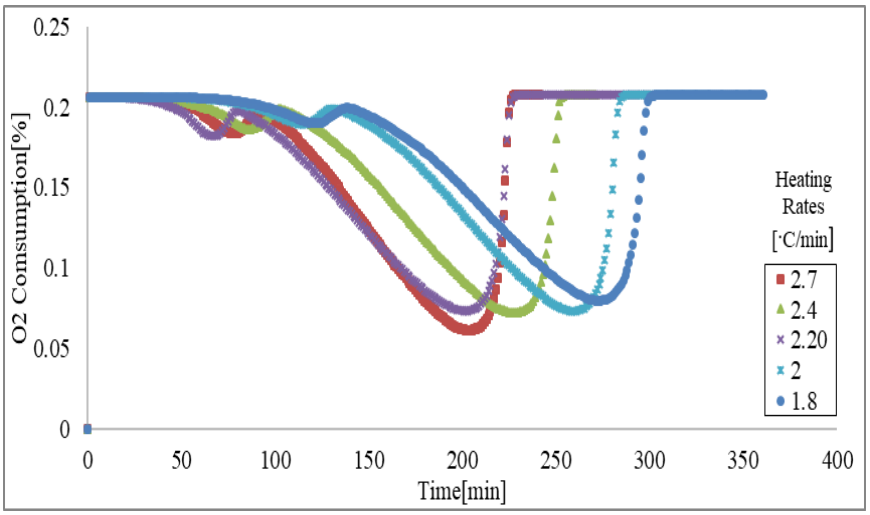

Figure 4.34: Oxygen consumption rate for all heating rates.

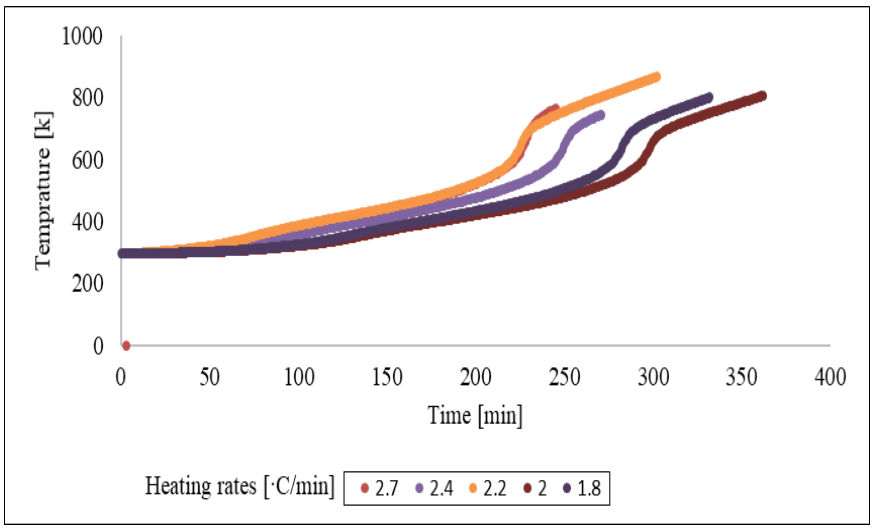

Figure 4.35: Temperature rate for all heating rates.

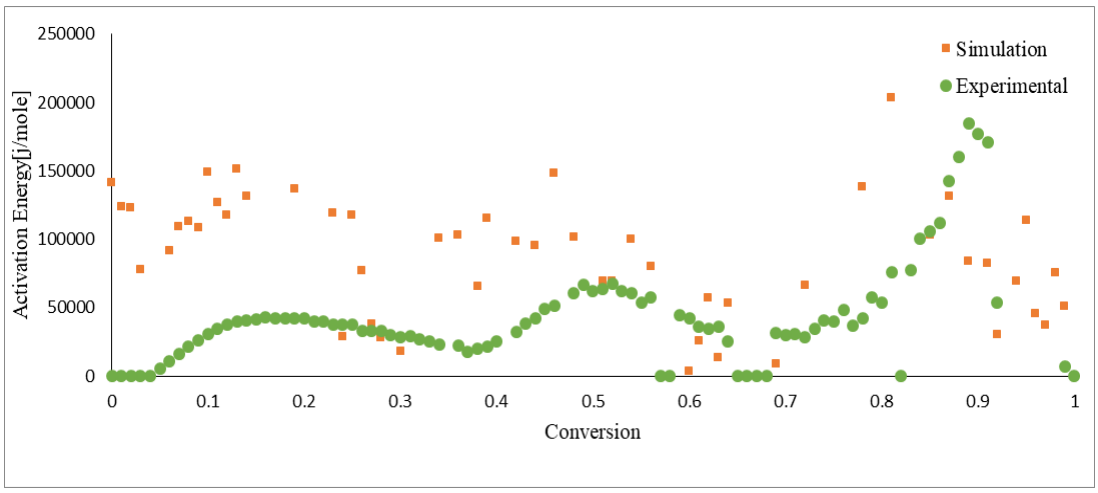

Figure 4.36: Isoconversional fingerprints compared.

Eventually, it would be valuable to get an idea of the approximate phase in which each reaction takes place. In this way, the governing reaction can be realized, and reactions happening in the most essential phases, namely HTO and LTO, can be estimated and optimized. Figure 4.37 shows that throughout the simulation, two main reactions seemed to play an important role in optimizing the process: carbon oxidation and pyrolysis.

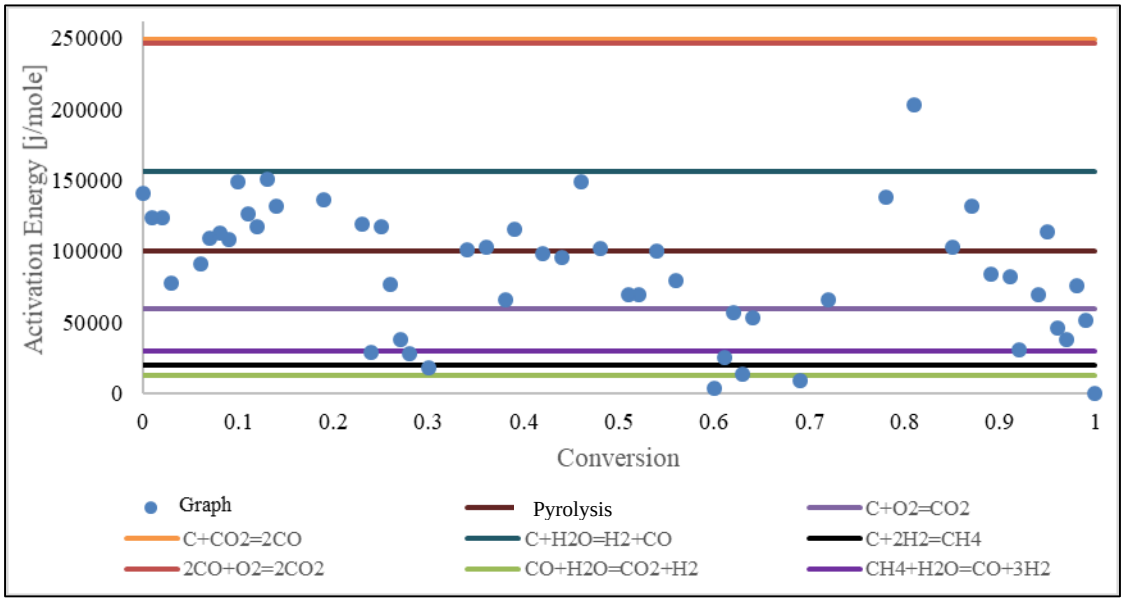

Figure 4.37: Reactions during gasification.

In the same manner, as reflected in Figure 4.37, these two reactions are the governing reactions in the overall process of the gasification of coal. The first reaction, pyrolysis, as mentioned before, is the initial step for starting the gasification. In this reaction, coal is decomposed into volatile matter and different gas components based on different parameters such as pressure and obviously coal characteristics while the temperature increases (Norouzieh et al., 2010). For the sake of simplicity, the kinetic parameters and chemical reaction methods used by Norouzieh et al. (2010) were also used in this study.

The second reaction that plays a critical role in this process is carbon oxidation. Seemingly, all the optimized parameters in the gasification process are directly affected by this reaction. Oxidation appears to take place in the later steps of gasification, approximately the HTO phase. Therefore, it can clearly be considered the most important reaction in gasification.

After coal undergoes pyrolysis, Carbon Monoxide, Methane, Hydrogen, and Carbon dioxide are produced, the first two of which are the main products. Therefore, the following reactions should have Carbon and Hydrogen as reactants.

Generally speaking, all the LTO and HTO mechanisms, which start from 0.4 to 0.8 conversions and are the most important, are two important reactions that govern the gasification process mentioned before. Therefore, to optimize the simulation, it is vital to enter the parameters and conditions related to these two reactions with the highest possible accuracy.

5. CONCLUSIONS AND RECOMMENDATIONS

Increasing demands for the implementation of alternative energy resources raise the need for innovative applications of conventional resources. Still, conventional resources are preferable since they are economical and abundant. Out of all fossil fuels, coal and asphaltite are intriguing ones since coal consumption still ranks among the first, and asphaltite is an abundant worldwide resource that can be used in different industries. The deposits are observed frequently in America, Australia, Sweden, Turkey, Argentina, Russia, and Iran (Gordadze et al., 2018)

On the other hand, environmental issues necessitate developing innovative methods of using these resources. First, emissions of greenhouse gases and other pollutants associated with utilization should be minimized, if not eliminated. Therefore, underground gasification is an exciting option.

Gasification itself is a combustion process; partial in a sense, abundance or lack of oxygen controls the process. Both asphaltite and coal have complex structures, which make it difficult to determine their kinetic parameters; therefore, in conducting these experiments, the aim is first to realize the behavior of coal and asphaltites in the combustion process. In this work, isoconversional methods are used for kinetic analysis. This analysis reveals activation energy changes with conversion, which is called isoconversional fingerprint. In this signature, it is vital to check for the reactions of low and high-temperature oxidation. Ramped temperature oxidation experiments of both coal and asphaltites at different heating rates are conducted. Isoconversional fingerprints were obtained and compared. In addition, the experiments are modeled using the STARS module of the CMG simulator.

The coal sample used is from Soma, and the asphaltite sample is from Şırnak. A total of 9 experiments were conducted, 5 of which were conducted on coal and four on asphaltite samples at different heating rates. Syngas concentrations and temperature in the reactor were collected. From the raw data, the following conclusions were reached:

- Two peaks in temperature, consumption, and production rates reflect the LTO and HTO reactions.
- While in Şırnak asphaltite and crude oil, the LTO reactions start at nearly 500 K; they start at 450 K in the case of Soma coal, which shows the high levels of volatile matter in coal.
- Carbon dioxide production in asphaltite is nearly twice that of coal.
- Oxygen consumption is higher in asphaltites in the LTO phase, which deals with lighter and intermediate structures. Therefore, this suggests that in this phase, there may be more parallel, multi-step, and complex reactions that should be addressed.
- As long as the desire is to compare oxygen consumption and carbon dioxide production, HTO reactions are identical; nevertheless, in LTO reactions, the consumption of oxygen is more than carbon dioxide production in both cases. This suggests that oxygen addition reactions occur.
- After mathematical calculations, regressions, and analysis using isoconversional methods, activation energy is obtained at different conversions. The data was analyzed using both O_2 consumption and CO_2 production data.

Taking O_2 consumption analysis into consideration:

- In general, an isoconversional fingerprint reveals two negative activation energy sections. These are usually associated with shifts in the reaction pathways. Similar behavior is observed in oil combustion but only at the early conversions. Repeated shifts reveal a more complex and different behavior compared to oil and coal.
- Thus, asphaltite behavior is very complex to analyze. It is extremely difficult, if not impossible, to deconvolve with isoconversional analysis. In the first stages until 0.45 conversion, it shows similar behavior with oil; however, between 0.4 and 0.6, there is no certain similarity neither with coal nor with oil. Therefore, this region, which deals with reactions consisting of tar formation, includes more multi-step parallel reactions that are unknown (Aksogan Korkmaz and Ozbas, 2017; Tonbul et al., 2009). Eventually, HTO reactions and Coal and crude oil, which are studied by Cinar (2011) and Glatz (2011), seem to have almost the same trend except for the intermediate phase

between 0.4 and 0.8. For crude oil, between 0.4 and 0.8, a moderate increase is observed in Cinar's (2011) study, whereas for coal, there is a decrease followed by an increase.

- Also, coal gasification generally needs more energy, which in the first phase is due to higher volatile matters stated by Çakal et al. (2007), Verma et al. (2020), and Femosso et al. (2009), and in the other stages comes from other elements like magnesium (Glatz, 2011; Nemanova et al., 2014; Jayaraman and Gokalp, 2015).

Taking carbon dioxide results shows:

- Generally speaking, this data shows more consistent results.
- The activation energy changes of asphaltite are similar to those of coal. Moreover, the general changes in both cases are almost similar, which means that reactions that lead to CO_2 production are similar.

CO_2 production and O_2 consumption are compared for both cases, and the results are as follows.

- For the asphaltite case, oxygen addition occurs with the production of CO_2 in the first stages of gasification, yet oxygen addition is not observed during and after HTO reactions.
- For coal, oxygen addition is limited during the production of carbon dioxide.
- CO_2 production reactions and mechanisms are probably the same in both samples. These reactions mainly involve carbon content directly reacting; as a result, the carbon contents of intermediate reactants in asphaltite and coal samples seem to be similar.

In the last step of this study, coal gasification is modeled using the CMG Stars module. The reservoir is a 4-layered radial reservoir with a length of 5.75 and a varying radius of 1.5, 3.2,4.2, and 11 for each layer. The four layers are defined as the kinetic cell, kinetic cell wall, the space between the cell and furnace, and the furnace. Kinetic parameters are estimated based on the study of Norouzieh et al. (2010) and should be updated and changed regularly to optimize the results. Reactions also are input based on the same study (Norouzieh et al., 2010). The kinetic parameters optimized in this study are shown in Table 5.2. It is noteworthy to mention that in this study, the aim is not to take a perfect match but firstly to validate the results of experimental and

theoretical data and then to get an idea of the governing reaction in each stage of gasification and reproduce experimental trends The results obtained from the model show compatibility with the experimental results namely conversion, temperature rate, and also activation energy changes.

- The scale differences resulting in these sections may be due to kinetic parameters such as reaction enthalpy.
- Among all the reactions involved in the gasification process of coal, pyrolysis, and carbon oxidation play the most important role in the gasification process. In this part, as was estimated when discussing the activation energy, carbon dioxide production, and oxygen consumption graphs, it was approved that carbon oxidation reaction takes place in the HTO reactions in nearly the last stages of gasification.

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- **Dorreh, E.** Kinetic Analysis of Combustion Characteristics of Asphaltites. International Graduate Research Symposium, May 16-18, 2023.