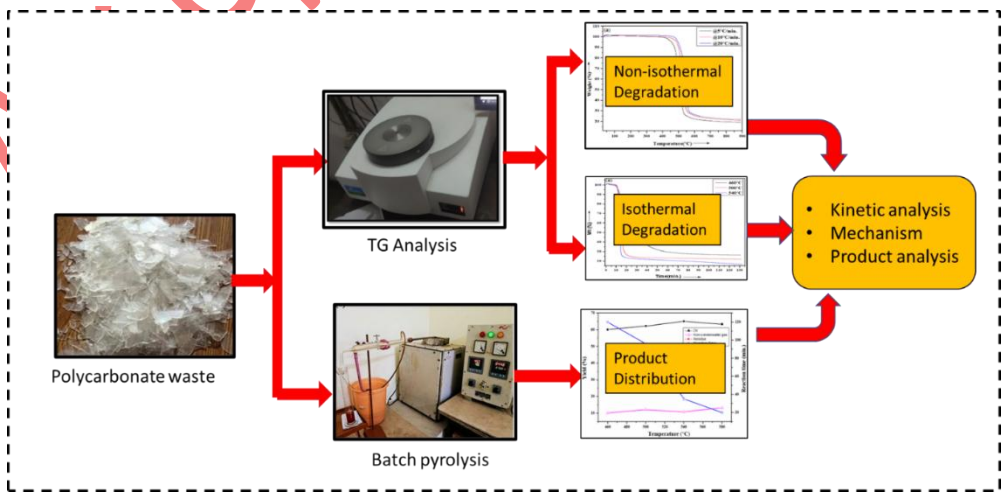
Valorisation of waste polycarbonate through pyrolysis: Kinetic analysis and batch pyrolysis studies

Abstract

The widespread use of polycarbonate in electrical and electronic equipment has contributed to the rapid accumulation of waste electrical and electronic equipment, posing significant environmental challenges. Sustainable recycling technologies are therefore essential for effective resource recovery. In this study, the isothermal and non-isothermal degradation kinetics of waste polycarbonate were investigated using model-fitting and model-free methods (KAS, FWO, and STR) to support pyrolysis reactor design. Batch pyrolysis was performed at different temperatures, and GC-MS and FTIR characterized the resulting pyrolytic oil. Non-isothermal degradation resulted in weight losses of ٨١٪, ٧٩٪, and ٧٧,٥٪ at ٥, ١٠, and ٢٠ °C/min, respectively, within the temperature range of ٤٦٠–٥٤٠ °C, and followed an F٣ mechanism with an activation energy of ١٤٢ kJ/mol. The reaction orders at ٤٦٠, ٥٠٠, and ٥٤٠ °C were ١,٣٥٥, ١,٤١٥, and ١,٠٢٥, respectively, based on Avrami (AVM) theory. Isothermal degradation of polycarbonate caused ٧٤٪, ٧٨٪, and ٨٣,٥٪ weight loss at ٤٦٠, ٥٠٠, and ٥٤٠ °C, respectively, and followed an F١ mechanism with an activation energy of ٣٢,٤٤٤ kJ/mol. Polycarbonate exhibited optimum pyrolysis performance at a heating rate of ٢٠ °C/min under non-isothermal conditions and at ٥٠٠ °C under isothermal conditions. Batch pyrolysis produced a maximum oil yield of ٦٥,٠٥٪ at ٥٤٠ °C, and the oil contained alkanes, alkenes, aromatic hydrocarbons, and oxygenated compounds as confirmed by FTIR and GC-MS analyses. This research work aims to design a framework for the pyrolytic degradation kinetics and reaction mechanism, and to develop a standard pyrolytic degradation procedure for the production of pyrolytic oil from waste polycarbonate, highlighting the valorisation of waste polycarbonate and recycling of the waste polycarbonate, making a substitute for fuel oil.

Keywords: Waste polycarbonate, pyrolysis, Non-isothermal degradation, kinetic analysis, batch studies

Graphical Abstract



١ Introduction

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The pollution due to waste plastic is significantly threatening to the global environment. Poly (bisphenol A carbonate) is one of the most widely used thermoplastics [١]. Poly (bisphenol A carbonate) is widely used in the body framework of televisions, computers, mobile phones, refrigerators, and other electrical appliances. In addition to these, poly (bisphenol A carbonate) is also used in large amounts as a raw material for the production of different types of bottles and food-storage containers [٢, ٣]. It is also used in automotive and transportation components, construction, manufacturing, packaging, medical instrumentation, optical media, electronics, audio-visual equipment, laser-optical data storage systems, CDs, DVDs, bulletproof windows, and food and mineral-water containers [٤].

The huge use of Poly (bisphenol A carbonate) (PC) in different fields forces a large amount of production of Poly (bisphenol A carbonate). It has been estimated that the global polycarbonate market already reached USD ٢٥,٠ billion in ٢٠٢٥; it is expected that it will reach a production value of ٢٥,٩ billion in ٢٠٢٦ at the end of ٢٠٢٦; further, it is predicted that it will reach up to USD ٣٦,١ billion by ٢٠٣٣, with a compound annual growth of ٤,٩٪ in the period of ٢٠٢٦–٢٠٣٣ [٥]. As a result, the production rate of Poly (bisphenol A carbonate) increases proportionally to the waste generation rate of Poly (bisphenol A carbonate [٦]. But the increase rate of waste production of polycarbonate is always higher than the rate of disposal of the PC waste because the PC wastes are resistant to complete degradation. This trend of rate of disposal surplus the waste PC in every annual estimation. As a result, this waste accumulates day to day; the role of polycarbonate waste production in environmental pollution is significant. PC is more sensitive to photodegradation, which causes the release of pollutants. This process can lead to the formation of toxic pollutants such as bisphenol A (BPA), which may persist in ecosystems because of its resistance to degradation [١]. The use of PC has also been associated with increased rates of prostate and breast cancer, reproductive problems, heart disease, and attention deficit hyperactivity disorder [٦].

Rapidly changing technology and the short life cycle of the items manufactured from these plastics led to their discharge to the environment as waste and constitute an important fraction of waste electrical and electronic equipment (WEEE). The recycling of WEEE is difficult because it contains different materials such as metals, glass, and plastics [٧]. Several plastic management methods, including landfilling, incineration, combustion, recycling, etc., have been applied for the disposal of waste plastics [١]. Landfill treatment also faces problems such as long-term occupation of land resources and destruction of soil structure, while BPA and other chemicals may migrate into groundwater and soil under humid conditions, potentially affecting aquatic ecosystems and crop growth. Chemicals in landfills may also inhibit soil microbial activity, reduce soil fertility, and affect plant growth [٨]. Incineration is a relatively temporary solution that may result in the release of toxic airborne pollutants or harmful substances and contribute to excessive carbon emissions [١]. PC on incomplete combustion produces toxic gases that cause air pollution. Similarly, incomplete incineration also releases toxic gases that cause air pollution. The incomplete incineration of the PC also produces toxic residue which on addition with soil and water body cause soil and water pollution [٨]. The mechanical recycling process, like grinding and reshaping of the PC, loses the quality of recycled products. As the efficiency of the recycled products decreases. As a result, the importance of the products decreases [٩]. Like the mechanical recycling process, the

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thermomechanical recycling process also shows negative impacts on the mechanical and physical properties, which restrict its application for the recycling of the waste PC. Chemical recycling processes such as solvolysis and reduction (hydrogenation and hydrosilylation) are significant and promising methods for the conversion of waste PC to various valuable products like phenols, alcohols, and alkanes [١]. However, the chemical recycling process requires specific experimental conditions, expensive energy, and chemical reagents to produce effective valuable products. As a result, this method is costly. In addition to this, these chemical recycling methods are selective. These challenges bring the method to backfoot [٩]. Therefore, there is an urgent need for effective valorisation and disposal methods for the conversion of the waste PC.

The above-mentioned problems in various methods can be solved by the implementation of the pyrolysis process, which can convert the waste PC into valuable products. In addition to these merits, the pyrolysis process also provides an effective and economical method for valorisation of the waste PC and reduces the waste PC. However, there is a need for improvement of the pyrolysis process. For the improvement of the pyrolysis process, there is a need for a kinetic mechanism study, a standard, effective pyrolytic process, and analysis of the pyrolytic products obtained by the pyrolysis of PC [٧].

Several studies have been completed regarding the kinetic mechanism and pyrolytic conversion of PC. Al-Hakami et al. reported on the kinetic mechanism, thermodynamic analysis, and pyrolytic degradation of PC using TGA and Py-GC/MS. The average activation energies determined by the KAS, FWO, and Starink isoconversional methods were ٢٤٥,٨١, ٢٣٥,٣٦, and ٢٤٩,٩٩ kJ mol^{-1}, respectively [٤]. Siddiqui et al. investigated the non-isothermal pyrolysis kinetics of polycarbonate (PC) using thermogravimetric analysis at different heating rates and applied both model-free (isoconversional) and model-fitting methods.
The activation energy calculated by the Tang and KAS integral methods varies from ١٤٦ kJmol$^{-١}$ to ١٨٩ kJ mol^{-1} with respect to the conversion. The activation energy calculated by the Friedman differential method also varied from ١٥٤ kJmol$^{-١}$ to ٢١٥ kJ mol^{-1}. This variation indicates that the composition of the PC is complex in nature. Among the kinetic models evaluated, the autocatalytic model provided the best fit, with reaction orders of n = ١,١٥ and m = ٠,٤٦, an average activation energy of ١٩٥,٩ kJ mol^{-1}, and a pre-exponential factor of ٦,٠٦ × ١٠^{12} min^{-1} [٧]. Varol et al. investigated the pyrolysis kinetics and thermal decomposition behaviour of polycarbonate using TGA-FTIR under a nitrogen atmosphere. The thermal decomposition occurred mainly in the temperature range of ٤٢٥–٦٠٠ °C, with an overall reaction order of ١,٥. The average activation energies determined by the Kissinger, Friedman, Flynn–Wall–Ozawa (FWO), and Kissinger–Akahira–Sunose (KAS) methods were ١٥٠,٤٢, ٢٣٠,٧٦, ٢١٦,٩٧, and ٢١٨,٥٦ kJ mol^{-1}, respectively [١٠]. Kitahara et al. investigated the thermal decomposition kinetics of poly(bisphenol A carbonate) (PC) using infrared image furnace–ion attachment mass spectrometry. Assuming first-order kinetics, the activation energy for PC decomposition and BPA formation was determined to be ١٣٣,٢ kcal mol^{-1} under a nitrogen atmosphere, whereas it decreased to ٨٦,٥ kcal mol^{-1} under oxidative conditions. This decrease in the activation energy confirms that the presence of oxygen initiates the thermal decomposition of PC to form BPA [٢].

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Tagle et al. found that the thermal degradation of polycarbonates with aromatic side groups follows a mechanism similar to that of polycarbonates, which involves the rearrangement of the carbonate group to a carboxylic group that is placed in the ortho position to an ether linkage, which leads to crosslinking. The presence of R groups attached to the aromatic side ring does not influence the thermal stability or the degradation mechanism [١١]. Zhang et al. investigated the thermal degradation mechanism of polycarbonate using quantum chemical calculations, showing that decarboxylation and carbonate/alkyl bond cleavage are important initial degradation pathways. The degradation mainly produced phenolic compounds, including phenol and bisphenol A, together with CO_2 and CO, while radical-assisted reactions promoted bond cleavage and the formation of secondary products such as dibenzofuran and xanthone [١]. The study by Jang and Wilkie revealed that the thermal degradation of polycarbonate proceeds mainly through cleavage of the isopropylidene linkages and hydrolysis/alcoholysis and rearrangement of the carbonate linkages. Based on bond dissociation energies, methyl scission of the isopropylidene linkage was proposed to occur preferentially during chain scission, followed by further degradation reactions that contribute to the formation of various volatile products [١٢]. Tai et al. investigated the pyrolysis mechanism and product evolution of polycarbonate using a carbonate dimer as a model compound through quantum chemical calculations. The study identified decarboxylation as the initial degradation pathway, followed by C–CH_3 and C–O bond scission, and showed that H radicals significantly promote these reactions. The degradation products mainly included phenolic compounds such as phenol and bisphenol A, together with CO_2 and CO, while dibenzofuran and xanthone were formed through secondary reaction pathways [٨]. According to McNeill and Rincon, some cyclic oligomers of bisphenol A carbonate and different phenol structures with masses of less than ٢٢٨ are produced by following a homolytic chain scission mechanism during the thermal degradation mechanism of polycarbonate using thermal volatilisation analysis under nitrogen [١٣, ١٤].

Grause et al. investigated the pyrolysis of poly (bisphenol A carbonate) at ٤٨٠ °C under a nitrogen atmosphere. The pyrolysis produced mainly solid residue, along with gaseous and liquid products. The gaseous fraction consisted predominantly of CO_2 and CO, while the low-boiling fraction contained mainly phenols and small amounts of other aromatic compounds. The formation of substantial high-boiling products and solid residue indicated the occurrence of secondary reactions during the pyrolysis of polycarbonate [١٥]. Al-Hakami et al. reported from Py-GC/MS analysis that phenolic compounds were the dominant components of the oil obtained under non-catalytic pyrolysis conditions, indicating that phenolic compounds are the major products formed during the thermal decomposition of polycarbonate [٤]. According to Huang et al., the thermal degradation of bisphenol A polycarbonate proceeds mainly through hydrolysis, with homolytic cleavage and rearrangement acting as competing pathways. The products, such as carbon dioxide, bisphenol A, and ١,١-bis(٤-hydroxyphenyl) ethane, are produced as major products, while products like carbon monoxide, methane, phenol, alkyl phenols, ether compounds, and phenyl-containing carbonates are produced as minor products. The bond present between the methyl carbon and the carbon atom and the bond present between the oxygen atom and the carbonyl carbon cause the initial thermal degradation of polycarbonate [١٦]. According to Davis et al., during the thermal degradation of polycarbonate, reactions like

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the degradation of the carbonate linkages are followed by hydrolysis and condensation reactions. The products, such as CO_2, phenol, and bisphenol A, along with smaller amounts of CO, CH_4, alkyl phenols, and diphenyl carbonate, are formed as major products [١٧]. Day et al. reported that the rate of volatile products formed during the pyrolysis of PC at ٧٠٠°C is lower than at ٩٠٠°C. The yield of products like carbon dioxide, phenol, ٤-methylphenol, and bisphenol A is higher at a pyrolytic temperature of ٩٠٠°C than at ٧٠٠°C [١٨]. Li et al. reported that the oxygenated compounds are formed as major products. About ٩٣,٤٪ of the total chromatographic area, ٨٩,٥٪. is phenolic compounds. Bisphenol A (BPA) (٤٢,٢٤٪) is the major individual product, with ١١,٩٣٪ phenol and ٧,٤٩٪ ٤-ethylphenol of the total oil production. The production of BPA is due to cleavage of the carbonate linkage. The secondary responsible for the formation of the products like lighter phenols and aromatic compounds [١٩]. Siddiqui et al. reported that during thermal degradation of the PC, gaseous products like CO_2, CO, and CH_4, along with liquid products that contain the compound like phenol, substituted phenols, and bisphenol A (BPA). The rate of production of the volatile products and substituted products increases, while the rate of production of BPA decreases with pyrolytic temperature [٧]. Montaudo et al. reported that the initial stage of polycarbonate thermal degradation, occurring at approximately ٤٠٠–٥٠٠ °C, involves the formation of cyclic oligomers through intramolecular exchange reactions, along with hydrolysis reactions that generate phenolic end groups and CO_2. At higher temperatures (٥٠٠–٧٠٠ °C), further molecular rearrangements and decomposition of the polycarbonate structural units occur, leading to the formation of phenyl and isopropenyl end groups, dibenzofuran, xanthone, and fluorenone structures. These thermally rearranged aromatic structures subsequently undergo aromatization and cross-linking, resulting in the formation of a graphite-like charred residue [٢٠]. Antonakou et al. reported that pyrolysis of polycarbonate at ٦٠٠ °C produced ٥٠–٦٠ wt.% liquid, ١٥–٢٠ wt.% gaseous, and ٢٠–٣٠ wt.% solid products. The liquid fraction was mainly composed of phenolic compounds, with a phenolic selectivity of ٧٠,٧٧ area%. Bisphenol A (BPA) constituted ٢٧,٤٤ wt.% of the organic liquid fraction obtained from model polycarbonate and ٤٠,٠٧ wt.% from commercial CD-derived polycarbonate. The gaseous products mainly consisted of CO_2, CO, H_2, and CH_4, while the liquid fraction contained phenol and various substituted phenolic compounds. These findings demonstrate the potential of polycarbonate pyrolysis for recovering valuable chemical products, particularly phenolic compounds and BPA [٢١]. Varol et al. reported that the evolved gases during pyrolysis of polycarbonate mainly consisted of CO_2, along with smaller amounts of CH_4, CO, H_2O, and other oxygen-containing compounds such as aldehydes, ketones, and carbonyls [١٠]. Kitahara et al. reported that the thermal decomposition of poly(bisphenol A carbonate) produced several phenolic and aromatic compounds, including phenol, methylphenol, ethylphenol, ptropylidenephenol, propylphenol, ethylbenzene, propylidenebenzene, propylbenzene, and bisphenol A (BPA) [٢].

Despite substantial research on the thermal pyrolysis of polycarbonate (PC), several important gaps remain in the existing literature. Comparative investigations of PC degradation behaviour and mechanisms under different heating rates and temperature ranges are still limited. In addition, most previous studies have estimated the activation energy using a single kinetic method, which may not adequately represent the complex degradation behaviour of polymers. A comprehensive evaluation using multiple kinetic approaches is therefore essential to obtain

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reliable kinetic parameters, including the activation energy, pre-exponential factor, and reaction model. Such kinetic parameters are particularly important for understanding the degradation mechanism, predicting the thermal behaviour of PC, determining suitable operating conditions, designing and scaling up pyrolysis reactors, and optimising the conversion of waste PC into value-added products. Furthermore, comprehensive kinetic studies integrating both isothermal and non-isothermal conditions and employing model-fitting as well as model-free methods are scarce. Although phenolic compounds and bisphenol A have been widely identified as major products of PC pyrolysis, detailed investigations of the composition and evolution of pyrolytic oil at different pyrolysis temperatures remain insufficient.

Therefore, the present study aims to address these research gaps through a systematic investigation of the thermal degradation kinetics and product characteristics of waste PC. The novelty of this work lies in the comprehensive evaluation of PC degradation using multiple kinetic approaches under both isothermal and non-isothermal conditions, combining model-fitting and model-free methods to establish reliable kinetic triplets and elucidate the underlying reaction mechanisms. In addition, the thermal degradation behaviour of the raw PC and the chemical composition of pyrolytic oils obtained from semi-batch pyrolysis at different temperatures are systematically investigated. The study of the kinetic mechanism with pyrolytic product analysis helps to understand the reaction mechanism and optimise experimental conditions for the valorisation of the waste PC through pyrolysis. The optimised experimental conditions, kinetic mechanism, and pyrolytic product analysis help to design a suitable reactor for the valorisation of the waste PC.

٢ Materials and methods

٢,١ Material

The collected waste compact disc is broken into small pieces with a hammer, then ground by a domestic grinder into powder form. The powdered PC is filtered using a No. ١٨ sieve to maintain a uniform particle size of around ١mm.

٢,٢ Methods

٢,٢,١ *Analysis of feedstock*

Different types of ASTM standard procedures are used for the proximate analysis of the waste polycarbonate sample: ASTM D٤٤٤٢- moisture content, ASTM D٣١٧٢- volatile matter, ASTM D٣١٧٧- fixed carbon, ASTM D٣١٧٥- ash content. The ultimate analysis of the polycarbonate is conducted by a CHNS analyser. Bomb calorimetry is used to analyse the calorific value of waste polycarbonate.

٢,٢,٢ Thermogravimetric analysis

PerkinElmer Pyris Series Simultaneous Thermal Analyzer (STA) ٨٠٠٠ is used under both non-isothermal and isothermal conditions to get the TGA data for the non-isothermal and isothermal kinetic analysis. The non-isothermal experimental conditions are: initial temperature = ٣٠ °C, final temperature = ٩٠٠ °C, heating rate = ٢٠°C/min, nitrogen gas flow rate = ٢٠ ml/min. The isothermal experimental conditions: pyrolysis temperature = ٤٦٠°C, ٥٠٠°C, and ٥٤٠°C; reaction time = ٢ hours; heating rate for achieving pyrolysis temperature = ٤٠°C/min; nitrogen

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gas flow rate = ٢٠ ml/min. Both non-isothermal and isothermal thermogravimetry analyses were conducted three times to increase the consistency and reliability of the results.

٢,٢,٣ Batch pyrolysis study and product analysis

This work is an extension of my previous work [٢٢]. Like the batch pyrolysis of the previous work, the batch pyrolysis of this work is also conducted by a stainless-steel reactor having internal diameter of ٣٧ mm, external diameter of ٣١ mm, height of ١٤٥ mm. The reactor is a hollow tube having one closed end, and the other is open to release the gaseous products. The reactor is filled with waste polycarbonate powder is inserted to the vertical furnace which is connected with exterior electric source. The vertical furnace is connected with a Proportional-Integral-Derivative controller for temperature control. A K-type Cr-Al thermocouple within the reactor measures the temperature, while the Shimaden PID controller maintains ±٣,٦°C accuracy for the furnace temperature. In the pyrolysis trials, ٣٠ grams of feedstock are placed into the reactor and subjected to heating at ٤٦٠°C, ٥٠٠°C, ٥٤٠°C, and ٥٨٠°C. After collecting and weighing the condensable liquids and solid residues, the yield of non-condensable gases is calculated based on material balance. All experiments are conducted in triplicate to ensure reliability. Pyrolytic oil composition was disclosed using the GCMS-QP٢٠٢٠ NX (Shimadzu) gas chromatograph-mass spectrometer and Bruker Alpha FTIR spectrophotometer.

٢,٢,٤ Kinetic Analysis of Polycarbonate Thermal Degradation

For the thermal degradation of waste polycarbonate, the kinetic analysis is carried out employing fundamental kinetic equations for non-isothermal and isothermal processes.
For a non-isothermal process:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^{T} e^{-Ea/RT} dT = \frac{AEa}{\beta R} p(x) \qquad (١)$$

Here, p(x) is an empirical approximation, where x = Ea/RT
The conversion rate, heating rate, gas constant, temperature, activation energy, and pre-exponential factor are symbolised by α, β, R, T, Ea, and A, respectively [٢٣].
For an isothermal process:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_0^{t} k\, dt = k\, t + I \qquad (٢)$$

Where, k = Rate constant, and I = Integrational constant
According to Arrhenius's equation,

$$\ln k = \ln A - \frac{Ea}{RT} \qquad (٣)\ [٢٤]$$

At a specific temperature, the rate constant (k) can be determined by analysing the graph plotted between g(α) and time t, with the optimal value selected based on the highest coefficient of determination ($R^{٢}$). The slope and intercept derived from the linear relationship between lnk and the reciprocal of temperature (١/T) are utilised to calculate the activation energy and the pre-exponential factor in isothermal solid-state kinetic studies [٢٤]. The functions f(α) and g(α), which represent the reaction mechanism and integral form of the reaction model, respectively, for various solid-state reaction mechanisms, have been comprehensively documented in our earlier research [٢٣]. To calculate Ea and A in the non-isothermal kinetics study, three iso-conversional methods are applied. The model equations for

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these methods are summarised in Table ١, which are obtained by using the corresponding approximation in equation ١.

Table ١ lists different types of linear iso-conversional models [٢٥].

Iso- conversional model	Approximation value p(x) Where, $x = \frac{Ea}{RT}$	Equation	Plot
KAS	$\frac{e^{-x}}{x^2}$	$\ln(\frac{\beta}{T^2}) = \ln(\frac{-AR(1-\frac{2RT}{Ea})}{Ealn\alpha}) - \frac{Ea}{RT}$ (٤)	$\ln(\frac{\beta}{T^2})$ Vs $\frac{1}{T}$
FWO	$e^{(-2.315-0.4567x)}$	$\ln\beta = \frac{lnAEa}{1-\alpha} - 5.331 - 1.052(\frac{Ea}{RT})$ (٥)	$\ln\beta$ Vs $\frac{1}{T}$
STR	$\frac{e^{-1.0008\,x} - 0.312}{x^{1.92}}$	$\ln(\frac{\beta}{T^{1.92}}) = \ln(\frac{AEa}{1-\alpha}) - 0.312 - 1.0008(\frac{Ea}{RT})$ (٦)	$\ln(\frac{\beta}{T^{1.92}})$ Vs $\frac{1}{T}$

In the context of AVM theory, the equation used for establishing the order (n) of the thermal degradation of polycarbonate (PC) is.

$$\ln(-\ln(1-\alpha)) = \ln A - \frac{Ea}{RT} - n\ln\beta \quad (٧)\ [٢٣]$$

The pyrolysis index (I) is:

$$I = \frac{(dw/dt)_{max}}{t_{max}\Delta t} \quad (٨)\ [٢٤]$$

Where $(dw/dt)_{max}$ and t_{max} denote the maximum weight loss rate in per cent per minute and time in minutes at maximum reaction rate, respectively.

Δt is the required amount of time in minutes for the primary reaction, and mathematically, it is given: $\Delta t = t_f - t_i$

Where, t_i = Time in minutes at α = ٠,٠٥, t_f = Time in minutes at α = ٠,٩٥

٣ Results and discussions

٣,١ *Feedstock characterisation results*

The results of the proximate analysis of PC show that the feedstock contains ٨٢,٣٩٪ volatile material, ٠,٤٢٪ moisture, no ash, and ١٧,١٩٪ fixed carbon. Based on the ultimate analysis, the composition of the PC sample includes ٦٩,٦٨٪ carbon, ٥,٤٣٪ hydrogen, ٢٤,٨٪ oxygen, ٠,٠٩٪ nitrogen, and ٠٪ sulfur. Additionally, the calorific value of the material is determined to be ٣١,٩٧ MJ/kg.

٣,٢ Non-Isothermal and Isothermal Thermogravimetric Analysis

The TG-DTG curves of the PC, displayed in Figure ١, were recorded at heating rates of ٥, ١٠, and ٢٠°C/min under non-isothermal conditions, with temperatures ranging from ٣٠°C to ٩٠٠°C.

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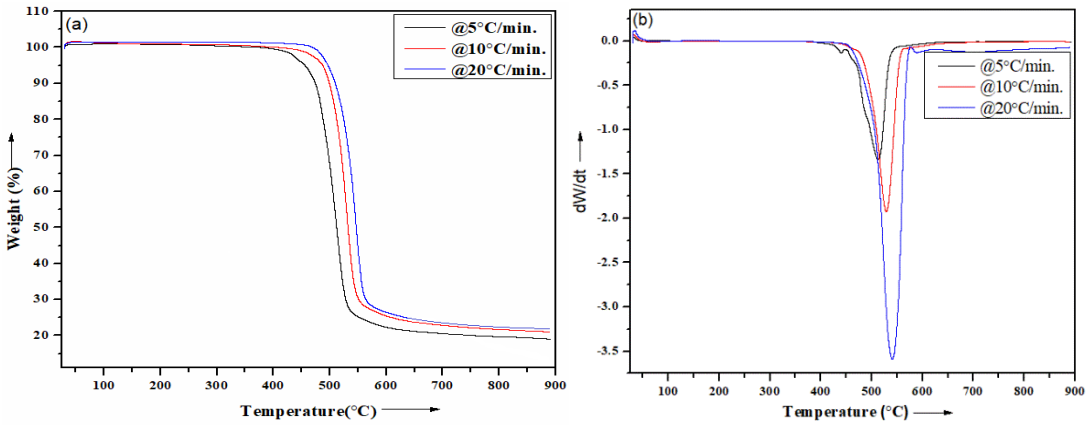


Figure ١ (a) TG and (b) DTG curves for the thermal degradation of polycarbonate under non-isothermal conditions

The TG-DTG plot makes it clear that there is a single-stage major degradation of PC. The weight loss of PC at ٥, ١٠, and ٢٠°C/min is ٨١٪, ٧٩٪, and ٧٧,٥٪, respectively. Following the ICTAC guidelines, the thermal degradation kinetics of the sample are more reliably determined at lower heating rates. The maximum extent of degradation, recorded at a heating rate of ٥°C/min, takes place predominantly within the temperature interval of ٤٦٠°C to ٥٤٠°C. Experiments are conducted at selected temperatures of ٤٦٠°C, ٥٠٠°C, and ٥٤٠°C, derived from the critical degradation range, to assess the reaction kinetics under isothermal conditions. These pyrolytic temperatures for isothermal degradation are selected based on the major thermal degradation temperature range in the non-isothermal thermal degradation. The degradation temperature range is also consistent with the degradation temperature of ٤٠٠–٥٠٠ °C reported in the literature by Montaudo et al. [٢٠]. Figure ٢ represents the TG-DTG curve of PC under isothermal conditions.

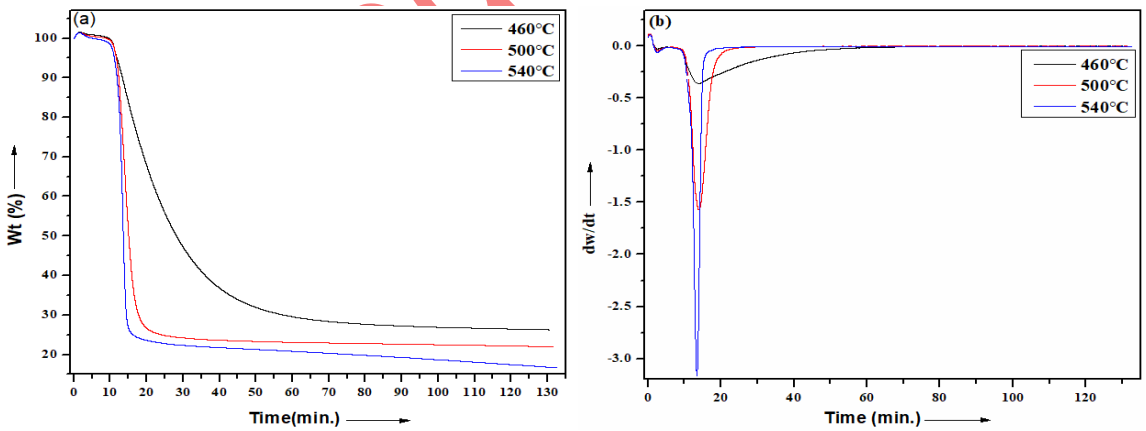


Figure ٢: (a) TG curve and (b) DTG curve of polycarbonate at isothermal conditions

From the data in Figure ٢, it is clear that under isothermal conditions, ٧٤٪, ٧٨٪, and ٨٣,٥٪ of PC's weight is degraded at ٤٦٠°C, ٥٠٠°C, and ٥٤٠°C, respectively.

٣,٣ Pyrolysis reaction kinetics

Kinetic analysis of polycarbonate degradation has been investigated in previous studies using model-free and model-fitting approaches, which provide valuable information on its thermal degradation behaviour, including activation energy, pre-exponential factor, reaction order, and

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the applicability of different kinetic models [٢, ٤, ٧, ١٠]. Model-free methods, such as the Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO), and Starink (STR) methods, enable the variation of activation energy with conversion to be evaluated without assuming a specific reaction model, whereas model-fitting methods allow the suitability of different reaction models to be assessed based on their correlation with the experimental degradation data. These thermogravimetry analysis data are useful for the pyrolysis reaction kinetics study.

٣,٣,١ Non-isothermal pyrolysis reaction kinetic analysis

The model fitting analysis shows that the activation energy increases with increasing heating rate. This increase in activation energy is due to thermal lag and the presence of impurities in the waste PC, arising during thermal degradation. Like activation energy, the Arrhenius factor also follows the same trend with respect to the increase of the heating rate, but the regression coefficient (R^2) shows negligible deviation with respect to the variation of heating rate. Overall, the variation of the value of the activation energy, Arrhenius factor, and regression coefficient is not significant and has no effect on the optimization of the kinetic triplet. To avoid such type of inconsistency, the average of activation energy, and Arrhenius

Factor is optimized. Table ٢ provides the results of activation energy, the Arrhenius coefficient, and the coefficient of determination, derived by using model-fitting analysis for the non-isothermal degradation of polycarbonate.

Table ٢. Kinetic parameters for non-isothermal pyrolysis using model fitting methods

Model	Activation energy (kJ/mol)	Arrhenius factor ($min.^{-1}$)	R^2
Nucleation model			
P_2	٢٣,١٤٤	٢,٠٥٤×١٠^{٧}	٠,٩٠١
P_3	١٥,٤٣٠	٤,٤٩٦×١٠^{٦}	٠,٩١٧
P_4	١١,٥٧٢	١,٩٥١×١٠^{٦}	٠,٩١٥
$P_{1,5}$	٦٩,٤٣٤	٦,١٠٥×١٠^{١٠}	٠,٩١٦
A_2	٣١,١٧٧	١,٩٩٥×١٠^{٨}	٠,٩٧٦
A_3	٢٠,٧٨٥	٢,٢١٢×١٠^{٧}	٠,٩٦٦
A_4	١٥,٣٧٢	٦,٤٨٠×١٠^{٦}	٠,٩٧٦
Geometrical contraction model			
R_2	٥٢,٣٣١	٣,٢٦١×١٠^{٩}	٠,٩٣٦
R_3	٥٥,١٢٧	٤,٦٢٤×١٠^{٩}	٠,٩٤٦
Diffusion model			
D_1	٤١,٣٣١	٣,٠٩٩×١٠^{٧}	٠,٩١٥
D_2	٤٤,٠٢٢	٣,٦٩٧×١٠^{٧}	٠,٩٢٥
D_3	٤٨,١٥٤	٣,٢٠٠×١٠^{٧}	٠,٩٠٤
D_4	٤٥,٣٢٨	١,٢٦٠×١٠^{٧}	٠,٩٠٥
Reaction order model			
F_0	٤٦,٢٨٩	١,٢٥٩×١٠^{٩}	٠,٩٠٣
F_1	٦٢,٣٥٣	٩,٦٣٠×١٠^{١٠}	٠,٩٠٤
$F_{1,5}$	٧٧,٥٩٠	٥,٥٤٢×١٠^{١٢}	٠,٩١٠
F_2	٩٦,٨٠٧	٨,٩٨٢×١٠^{١٤}	٠,٩١٦

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$F_{2,0}$	١١٨,١٩٠	٢,٥٤٣×١٠^{١٧}	٠,٩١٧
F_3	١٤١,٨١١	٩,٥٥٤×١٠^{١٩}	٠,٩٥٠
F_4	١٨٧,٤٦٨	٢,٠٠٩×١٠^{٢٥}	٠,٩٠٣
F_0	٢٣٥,٤٠٠	٥,٤٤٢×١٠^{٣٠}	٠,٩٠٧

The KAS, FWO, and STR model-free kinetic plots for the non-isothermal degradation of PC are presented in Figure ٣.

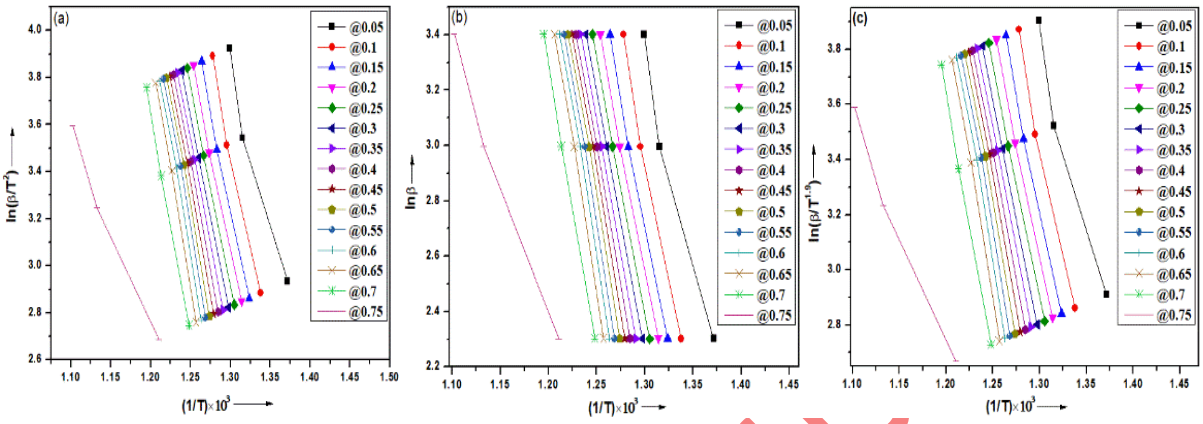


Figure ٣ Kinetic plots of KAS, FWO, and STR model-free methods for PC pyrolysis

Table ٣ Kinetics parameters calculated by model-free methods for non-isothermal pyrolysis of Polycarbonate

A	KAS			FWO			STR		
	Ea (kJ/mol)	A (min.$^{-1}$)	R^2	Ea (kJ/mol)	A (min.$^{-1}$)	R^2	Ea (kJ/mol)	A (min.$^{-1}$)	R^2
٠,٠٥	١٠٧,٣٧٧	٣,٨٠٠×١٠^{١٣}	٠,٩٣٧	١١٩,٨١٢	٢,٤٧٨×١٠^{٨}	٠,٩٤٩	١٠٧,٨٧٥	١,١٥٨×١٠^{٧}	٠,٩٣٧
٠,١	١٣٦,١١٤	٢,٢٩٦×١٠^{١٥}	٠,٩٨١	١٤٨,٨١٤	١,٢٤٣×١٠^{١٠}	٠,٩٨٤	١٣٦,٦٢٢	٥,٤٦٩×١٠^{٨}	٠,٩٨١
٠,١٥	١٣٨,٤٥١	٢,١٧١×١٠^{١٥}	٠,٩٩٣	١٥١,٢٩١	١,٣٣٣×١٠^{١٠}	٠,٩٩٤	١٣٨,٩٦٥	٥,٧٤٢×١٠^{٨}	٠,٩٩٢
٠,٢	١٣٧,١٤٧	١,٢٥٢×١٠^{١٥}	٠,٩٩٦	١٥٠,٠٨٦	٨,٨١٢×١٠^{٩}	٠,٩٩٧	١٣٧,٦٦٤	٣,٧٤٤×١٠^{٨}	٠,٩٩٦
٠,٢٥	١٤٠,١٦١	١,٥٠٩×١٠^{١٥}	٠,٩٩٨	١٥٣,١٨٦	١,١٢٤×١٠^{١٠}	٠,٩٩٩	١٤٠,٦٨٢	٤,٧١١×١٠^{٨}	٠,٩٩٨
٠,٣	١٤٢,٧٩٨	١,٧٥٧×١٠^{١٥}	٠,٩٩٩	١٥٥,٨٩٩	١,٣٧٣×١٠^{١٠}	٠,٩٩٩	١٤٣,٣٢٢	٥,٦٨٧×١٠^{٨}	٠,٩٩٩
٠,٣٥	١٤٥,٩٨٦	٢,٢٧٠×١٠^{١٥}	٠,٩٩٩	١٥٩,١٥٣	١,٨٣٢×١٠^{١٠}	٠,٩٩٩	١٤٦,٥١٣	٧,٥٠٢×١٠^{٨}	٠,٩٩٩
٠,٤	١٤٩,١٧٣	٢,٩٥٩×١٠^{١٥}	٠,٩٩٨	١٦٢,٤٠٠	٢,٤٤٧×١٠^{١٠}	٠,٩٩٨	١٤٩,٧٠٢	٩,٩١٩×١٠^{٨}	٠,٩٩٨
٠,٤٥	١٥٣,٤٥١	٤,٥٩٦×١٠^{١٥}	٠,٩٩٧	١٦٦,٧٣٠	٣,٨٢٢×١٠^{١٠}	٠,٩٩٧	١٥٣,٩٨٢	١,٥٣٥×١٠^{٩}	٠,٩٩٧
٠,٥	١٥٧,١٠٦	٦,٤٣٥×١٠^{١٥}	٠,٩٩٥	١٧٠,٤٣٧	٥,٤٠٣×١٠^{١٠}	٠,٩٩٦	١٥٧,٦٤٠	٢,١٥١×١٠^{٩}	٠,٩٩٥
٠,٥٥	١٦١,٥٧١	١,٠١٢×١٠^{١٦}	٠,٩٩٤	١٧٤,٩٥١	٨,٤٧٥×١٠^{١٠}	٠,٩٩٥	١٦٢,١٠٧	٣,٣٤٣×١٠^{٩}	٠,٩٩٤
٠,٦	١٦٣,٨٥٤	١,١٠٩×١٠^{١٦}	٠,٩٩٣	١٧٧,٢٨٨	٩,٤٨١×١٠^{١٠}	٠,٩٩٤	١٦٤,٣٩١	٣,٧٠٨×١٠^{٩}	٠,٩٩٣
٠,٦٥	١٦٧,٢٦٨	١,٣٩٦×١٠^{١٦}	٠,٩٩٧	١٨٠,٧٦٢	١,٢٠٢×١٠^{١١}	٠,٩٩٧	١٦٧,٨٠٨	٤,٦٥٦×١٠^{٩}	٠,٩٩٧
٠,٧	١٥٧,٣٤٧	١,٩٩٧×١٠^{١٥}	٠,٩٩٨	١٧٠,٩٤٨	٢,٠٢٦×١٠^{١٠}	٠,٩٩٨	١٥٧,٨٩١	٧,٧٧٠×١٠^{٨}	٠,٩٩٨
٠,٧٥	٦٧,٩٥٢	٧,٦٢٣×١٠^{٨}	٠,٩٧٤	٨٢,٣٠٢	٣,٩٨٣×١٠^{٤}	٠,٩٨١	٦٨,٥٢٦	١,٥٢٦×١٠^{٣}	٠,٩٧٤
Average	١٤١,٧١٧	٤,١٦٣×١٠^{١٥}	٠,٩٣٧	١٥٤,٩٣٧	٣,٤٣٢×١٠^{١٠}	٠,٩٩٢	١٤٢,٢٤٦	١,٣٦٤×١٠^{٩}	٠,٩٩٠

Table ٣ reveals that the activation energy values from the KAS method (١٤١,٧١٧ kJ/mol), STR method (١٤٢,٢٤٦ kJ/mol), and the F_3-order-based model (١٤١,٨١١ kJ/mol) are closely aligned, suggesting that the non-isothermal degradation of polycarbonate is consistent with the F_3-order-based model, yielding an activation energy of around ١٤٢ kJ/mol. However, a notable

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discrepancy exists in the pre-exponential factor and R^2 values between the F٣-order-based model-fitting approach and model-free methods (KAS, FWO, and STR), highlighting the differences in assumptions and computational frameworks used by these techniques. From Tables ٢ and ٣, the A value ranges from ١,٣٦٤×١٠^{٩}-٩,٥٥٤×١٠^{١٩} min.$^{-١}$; similarly, the average $R^{٢}$ value ranges from ٠,٩٣٧-٠,٩٩٢. The order of reactions for the non-isothermal degradation of PC using the AVM theory (equation ٧) and Figure ٤ are ١,٣٥٥,١,٤١٥, and ١,٠٢٥ at temperatures ٤٦٠,٥٠٠, and ٥٤٠°C, respectively.

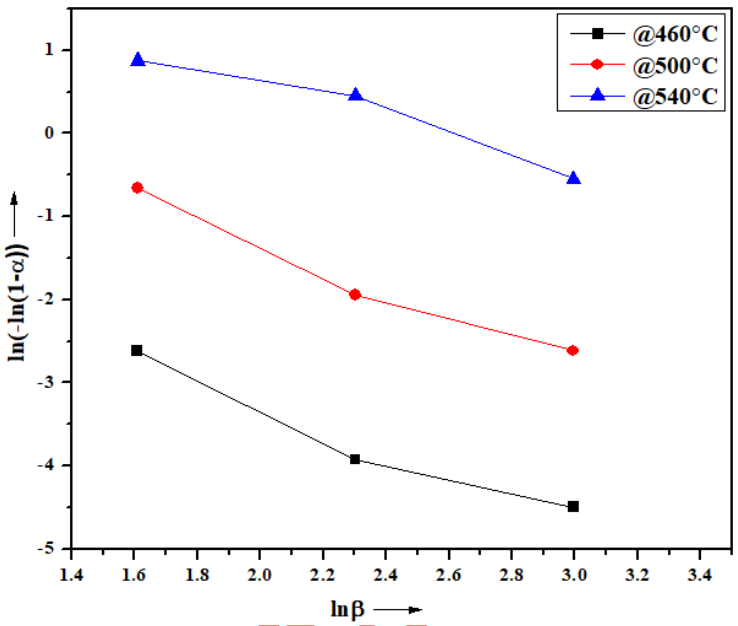


Figure ٤. Curves for the order calculation of polycarbonate at different temperatures

٣,٣,٢ Isothermal kinetic analysis

The thermal degradation of polycarbonate under isothermal conditions is investigated using several model-fitting methods. The coefficient of determination, activation energy, and Arrhenius constant values, which are derived from the data in Figure ٥, are summarised in Table ٤. The F١-order-based method stands out as the most accurate and precise approach for explaining the pyrolytic degradation of polycarbonate. This method demonstrates superior alignment with the experimental data, making it the most reliable approach for understanding the degradation kinetics in this context. Figures ٥(a) and (b) are drawn using equations ٢ and ٣ for the first-order reaction and the kinetic parameter during the isothermal degradation of PC, respectively. Equation ٢, the f(α) value, and Figure ٥(a) are used to get the K value. Equation ٣ can be used to generate a graph of lnK versus (١/T) with different model-fitting methods, providing the Ea and A values that correspond to the highest R^2.

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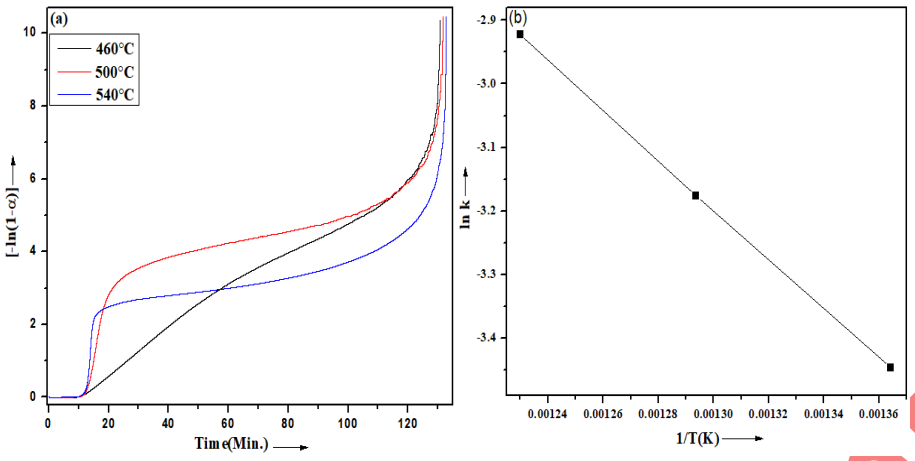


Figure ٥ (a) First-order reaction linear fitting and (b) kinetic parameter analysis for isothermal degradation of polycarbonate

Figure ٥(a) illustrates that the first-order-based method has the maximum coefficient of determination. However, using equations ٢ and ٣ with the f(α) value, the Ea and A values for all model fitting methods can be computed, and these values are shown in Table ٤.

Table ٤ Kinetic parameters using model-fitting methods for isothermal pyrolysis of PC

Model	Activation energy (kJ/mol)	Arrhenius factor (min.$^{-1}$)	R^2
Nucleation model			
P_2	٣٨,٩٨٣	١,١٠٨	٠,٩٨٦
P_3	٢٣,٦٣٩	٠,١٨٢	٠,٩٥٢
P_4	٣٢,١٩٦	٠,٢٦٠	٠,٧٥٣
$P_{1,5}$	٤٩,٥٢٥	٨,٨٠٩	٠,٨٩٧
A_2	٣١,١٣٨	١,٥٤٠	٠,٥٣٧
A_3	٢٧,٨٨١	٠,٧٨٦	٠,٩٦١
A_4	١٢,٧٦٠	٠,٣٠٠	٠,٧٢٦
Geometrical contraction model			
R_2	٢٨,٤٥١	٠,٤٧٤	٠,٧٢٠
R_3	٢٩,١٩٨	٠,٥١٢	٠,٨١٨
Diffusion model			
D_1	٣٠,٦٩٧	٠,٦٨٩	٠,٥٧٩
D_2	٣٠,٣٠٩	٠,٦٩٧	٠,٥٩٤
D_3	٣٠,٥٧٧	٠,٦٢٢	٠,٩٣٠
D_4	٢٩,٨٧٩	٠,٢٢٠	٠,٦٩٠
Reaction order model			
F_0	٢٦,٥١٧	٠,٣٢٠	٠,٦٤٥
F_1	٣٢,٤٤٤	٦,٥٢٣	٠,٩٩٩
$F_{1,5}$	٤٤,٧٥٤	٣,٣٢١×١٠^{2}	٠,٦٩٠
F_2	٥٩,٢٦٥	٥,٧١٧×١٠^{4}	٠,٥٦٠
$F_{2,5}$	٥٨,١٥٢	٢,٢٣١×١٠^{6}	٠,٥٨٤
F_3	٤٩,٣٣٣	٤,٩٢٨×١٠^{7}	٠,٦٥٢
F_4	٣٤,٥٠٣	٧,٧٩٢×١٠^{10}	٠,٦٣٢

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F_0	٢٨,١٤٨	٦,٥٨٢×١٠^{١٤}	٠,٧٣٩

As shown in Table ٤ and Figure ٥b, the F_1 (first-order) model-fitting method provides the most accurate representation of the isothermal degradation of polycarbonate, as evidenced by its highest R^2 value of ٠,٩٩٩. The isothermal degradation of polycarbonate gives an activation energy of ٣٢,٤٤٤ kJ/mol and an Arrhenius constant of ٦,٥٢٣ min^{-1} using this method.

٣,٣,٣ Pyrolysis Index Measurement

The maximum rate of pyrolysis and reaction time both affect the pyrolysis index (I). The pyrolysis performance increases with increasing pyrolysis index in terms of reaction rate [٢٤]. The isothermal and non-isothermal pyrolysis index for PC at various temperatures is computed by using equation ٨ and enumerated in Table ٥.

Table ٥ Results of Temperature-dependent PC pyrolysis index

Isothermal pyrolysis index					
T (°C)	**t_i (min.)**	**t_{max} (min.)**	**t_f (min.)**	**DTG_{max} (% $min.^{-1}$)**	**I (% $min.^{-3}$)**
٤٦٠	١١,٤٣	١٤,٣	٥٧,٨٠	٣٦,٠٠	٠,٠٥٤
٥٠٠	١١,٢٠	١٤	٢١,٣٦	١٥٨,٢٣	١,١١٢
٥٤٠	١٠,٩٦	١٣,٣	١٧,٠٠	٣١٥,٧٥	٣,٩٣٠
Non-isothermal pyrolysis index					
Heating rate	**t_i (min.)**	**t_{max} (min.)**	**t_f (min.)**	**DTGmax (% $min.^{-1}$)**	**I (% $min.^{-3}$)**
٥	٤٣,١٣	٤٩,٤٨	٥٦,٦٥	١٣٤,١٠	٠,٢٠١
١٠	٢٣,٦٠	٢٥,٩٠	٣٠,١٠	١٩٣,٧٠	١,١٥١
٢٠	١٦,٤٥	١٧,٨٤	٢٦,١٥	٣٥٩,١٠	٢,٠٧٥

From Table ٥, it is seen that with an increase in the heating rate, the pyrolysis index increases, which indicates that during the non-isothermal pyrolysis of polycarbonate, a large amount of volatile matter is released [٢٦]. The results in Table ٥ indicate that non-isothermal degradation is most efficient at a heating rate of ٢٠°C/min, while isothermal pyrolysis is most effective at the pyrolysis temperature of ٥٤٠°C.

٣,٣,٤ Results of batch pyrolysis

The graph of product yield percentages-temperature-reaction time is shown in Figure ٦. The batch pyrolysis of the polycarbonate at different pyrolytic temperatures produces different products, including condensable gases, residue, and non-condensable gaseous fraction. The condensable gases are condensed to liquid fuel, and the solid residue is collected after cooling. The liquid fuel and residue are weighed to calculate the percentage of yield. The percentage of yield of the non-condensable gas is calculated by subtracting the percentage of yield of liquid and residue from one hundred. The results of the yield of the liquid fuel, residue, and non-condensable gas are shown in the graph of product yield percentages-temperature-reaction time.

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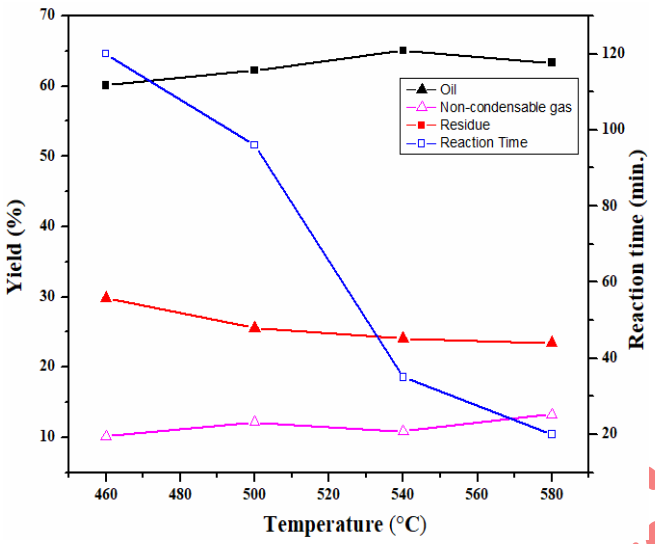


Figure ٦. Effect of temperature on product yields and reaction time

From the graph, it is seen that the oil yield is ٦٠,١٢٪, ٦٢,٢٣٪, ٦٥,٠٥٪, and ٦٣,٢٩٪ at temperatures of ٤٦٠°C, ٥٠٠°C, ٥٤٠°C, and ٥٨٠ °C, respectively. These results indicate that the yield of the fuel oil increases at temperatures of ٤٦٠°C, ٥٠٠°C, and ٥٤٠°C but decreases slightly at ٥٨٠ °C. The yield of residue is ٢٩,٧٧٪, ٢٥,٦٪, ٢٤,١٢٪, ٢٣,٤٢٪ at temperatures of **٤٦٠ °C, ٥٠٠ °C, ٥٤٠ °C, and ٥٨٠ °C, respectively. These results indicate that the yield of** residue decreases with an increase in temperature from ٤٦٠°C to ٥٨٠ °C. The yield of the non-condensable gas is ١٠,١٤٪, ١٢,١٧٪, ١٠,٨٣٪, and ١٣,٢٩٪, at temperatures of ٤٦٠ °C, ٥٠٠ °C, ٥٤٠ °C, and ٥٨٠ °C, respectively. These results indicate that the yield of non-condensable gas has no regular trend with pyrolytic temperature. The reaction time for the pyrolysis of polycarbonate is ١٢٠ minutes, ٩٦ minutes, ٣٥ minutes, and ٢٠ minutes, respectively. This results in a decrease in reaction time with an increase in the pyrolysis temperature. This decreasing trend of the reaction time with respect to the increase of the pyrolysis temperature indicates that higher temperatures accelerate the pyrolytic reactions, which cause faster thermal degradation of polycarbonate. Overall, the optimum temperature for the yield of pyrolytic fuel oil from the thermal degradation of the polycarbonate is ٥٤٠°C. **٣,٣,٥ Chemical composition of pyrolytic oils**

The pyrolytic fuel oil obtained from pyrolysis of the polycarbonate at different temperatures is subjected to GC-MS and FTIR analysis to confirm the presence of different compounds in the pyrolytic oils. The results of the GC-MS analysis of different pyrolytic oils obtained from polycarbonate at different temperatures are listed in Table ٦.

Table ٦ Results of the GC-MS analysis of pyrolytic oils

Temperature (°C) →		٤٦٠	٥٠٠	٥٤٠
Compound	**Formula**	**Area (%)**		
Saturated Hydrocarbons ($C_{٩}$-$C_{٢٠}$)		٢,٣١	٢,٨٤	٦,٧١
Nonane	$C_{٩}H_{٢٠}$	٠,١	٠,١١	٠,٦٢
Undecane	$C_{١١}H_{٢٤}$	٠,١١	٠,٢	٠,٣٧
٤,٥-dimethylnonane	$C_{١١}H_{٢٤}$	٠,٢	٠,٢٤	٠,٣٦
Dodecane	$C_{١٢}H_{٢٦}$	٠,١٥	٠,١٥	٠,٣٢
Tridecane	$C_{١٣}H_{٢٨}$	٠,٢٧	٠,٣٢	٠,٤٩

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Tetradecane	$C_{14}H_{30}$	٠,١٥	٠,٢	٠,٤٣
٢,٦,١١-trimethyl dodecane	$C_{15}H_{32}$	٠,٣٦	٠,٣٨	٠,٩٢
Pentadecane	$C_{15}H_{32}$	٠,٢٩	٠,٤	٠,٦٩
Heptadecane	$C_{17}H_{36}$	٠,٢٩	٠,٣	٠,٤٩
Eicosane	$C_{20}H_{42}$	٠,٣٩	٠,٥٤	٢,٠٢
Unsaturated Hydrocarbon (C_7-C_{14})		٢,٦٨	٣,٦١	٦,٥٦
٣-methyl-٢,٤-hexadiene	C_7H_{12}	٠,٢٤	٠,٥٩	٠,٦٥
Octene	C_8H_{16}	٠,١٢	٠,٣٢	١,١٢
Nonene	C_9H_{18}	٠,١٥	٠,٣٢	٠,٣٤
Decene	$C_{10}H_{20}$	٠,٤٦	٠,٤٨	١,٢٢
Undecene	$C_{11}H_{22}$	٠,٤٢	٠,٥٢	٠,٨٨
Dodecene	$C_{12}H_{24}$	٠,٢٤	٠,٢٥	٠,٤٨
Tridecene	$C_{13}H_{26}$	٠,٣٨	٠,٣٨	٠,٦
١-Tetradecene	$C_{14}H_{28}$	٠,٦٧	٠,٧٥	١,٢٧
Alicyclic (C_{10})		٦,٩٧	١٢,٧٥	١٨,٨٢
D-Limonene	$C_{10}H_{16}$	٦,٩٧	١٢,٧٥	١٨,٨٢
Aromatic hydrocarbon compound (C_7-C_{10})		٣٠,١١	٢٧,٠٢	٢٢,٩٣
Toluene	C_7H_8	٨,٧٠	٨,١٦	٧,٠١
Styrene	C_8H_8	١,٣٣	١,٠١	٠,٩
Ethylbenzene	C_8H_{10}	٤,٠١	٣,٤٧	٢,٩١
١,٣-dimethylbenzene	C_8H_{10}	٦,٩	٦,٠٩	٥,١٧
١-ethenyl-٤-methyl benzene	C_9H_{10}	٠,٦٣	٠,٥٤	٠,٤٤
α-Methyl styrene	C_9H_{10}	١,٨٩	١,٧٧	١,٦
١-ethyl-٣-methylbenzene	C_9H_{12}	٢,٨	٢,٦٦	٢,٥٥
Propyl benzene	C_9H_{12}	٠,٥	٠,٣٢	٠,٢٢
(١-Methylethyl) benzene	C_9H_{12}	٠,٨	٠,٧٣	٠,٦٩
p-(١-Propenyl)-toluene	$C_{10}H_{12}$	٠,٤	٠,٣١	٠,٢٤
o-Cymene	$C_{10}H_{14}$	٠,٦٢	٠,٥٢	٠,٤٢
١-methyl-٣-(phenylmethyl) benzene	$C_{14}H_{14}$	٠,٦٢	٠,٥٧	٠,٤٦
١,١'-(١-methylethylidene) bis-benzene	$C_{15}H_{16}$	٠,١٣	٠,١	٠,٠٩
١,١'-methylene bis [٣-methyl benzene	$C_{15}H_{16}$	٠,٧٨	٠,٧٧	٠,٢٣
Oxygenated compound(C_{14}-C_{26})		٥٧,٩٣	٥٣,٧٨	٤٤,٩٨
٤-Methyl-٢-phenylphenol	$C_{13}H_{12}O$	٤,٠٣	٣,٣٣	٢,٤٩
١-Ethyl-٣-phenoxybenzene	$C_{14}H_{14}O$	١,١٧	٠,٩٦	٠,٢٣
٤-(١-methyl-١-phenylethyl) phenol	$C_{15}H_{16}O$	٢٥,٩٥	٢٤,٣٥	٢٢,١
٢-(١,١-dimethylbenzyl) phenol	$C_{15}H_{16}O$	١٧,٣	١٦,٥	١٤,٢
٢-Methyl-٦-(١-methyl-١-phenylethyl) phenol	$C_{16}H_{18}O$	٣,٧٠	٣,٤٧	٢,٠٥
١-(١,١-dimethylethyl)-٤-phenoxy Benzene	$C_{16}H_{18}O$	١,١	٠,٩٣	٠,٣١
E-١٤-Hexadecenal	$C_{16}H_{30}O$	٠,٤٧	٠,٥٤	٠,٨٩
١-Hexadecanol	$C_{16}H_{34}O$	٠,١٩	٠,٣	٠,٦٢
Benzene acetic acid, α-methyl-٣-phenoxy-, methyl ester	$C_{16}H_{16}O_3$	٠,٣٩	٠,٣٥	٠,١٨
٣-[٤-(١,١-dimethylethyl) phenoxy Benzaldehyde	$C_{17}H_{18}O_2$	٠,٣٣	٠,٢٨	٠,٢٥

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Phthalic acid, ٣-methylphenyl phenyl ester	$C_{٢١}H_{١٦}O_{٤}$	٠,٩٨	٠,٧١	٠,٤٢
٢,٤-bis(١-phenylethyl) phenol	$C_{٢٢}H_{٢٢}O$	٢,٣٢	٢,٠٦	١,٢٤

According to Table ٦, the oils consist of alkanes, alkenes, alicyclic compounds, aromatic hydrocarbons, and oxygenated compounds, with trace levels of aldehydes and alcohols. The data in Table ٦ indicate that the pyrolytic oils formed at ٤٦٠°C, ٥٠٠°C, and ٥٤٠°C are composed of similar types of compounds. The amount of the different compounds present in different pyrolytic oils varies with pyrolytic temperature. The oxygenated compounds, aromatic hydrocarbons, and alicyclic compounds present in the pyrolytic oil act as major compounds, whereas the saturated and unsaturated hydrocarbons are minor products. A temperature from ٤٦٠°C to ٥٤٠°C leads to higher levels of alkanes, alkenes, and alicyclic compounds, and a reduction in aromatic hydrocarbons and oxygenated compounds, as supported by FTIR results. The distribution of oxygenated, aromatic, alicyclic, and aliphatic compounds in the pyrolytic oils is consistent with the complex decomposition pathways reported for polycarbonate pyrolysis. The predominance of oxygenated and aromatic compounds agrees with the reported formation of phenolic and other aromatic products, while the presence of aliphatic and alicyclic hydrocarbons indicates possible secondary transformations at elevated temperatures [١, ٢, ٨, ١٠, ١٥-١٧, ١٩-٢١].

Figure ٧ illustrates the FTIR spectra of pyrolytic oils produced from polycarbonate at various temperatures: ٤٦٠°C, ٥٠٠°C, and ٥٤٠°C. The spectra in Figure ٧ demonstrate that the characteristic peaks for specific functional groups are consistent across the oil samples, with similar wavenumbers. However, the variation in peak intensity implies that the oils possess similar chemical compositions, but the proportions of the components vary. The peaks at ٦٨٨ and ٧٤٨ cm^{-1} indicate aromatic C-H out-of-plane bending, while the peak at ١٠١٣ cm^{-1} is a confirmation of aromatic C-H in-plane bending. The C-H bending in monosubstituted aromatic compounds is related to the peaks obtained at ٦٨٨ and ٧٤٨ cm^{-1}. The C-H bending in disubstituted (meta) aromatic compounds is related to the peaks obtained at ٦٨٨ cm^{-1}. The C-H bending in disubstituted (ortho) aromatic compounds is related to the peaks obtained at ٧٤٨ cm^{-1}. The peak at ٦٨٨ cm^{-1} is attributed to alcoholic OH out-of-plane bending, while the ٧٤٨ cm^{-1} peak relates to methylene $–(CH_2)_n–$ rocking (where $n \geq ٣$). The C-C stretching in alkanes is reflected by the peaks at ٨٢٠, ١٠١٣, ١١٠٥, and ١١٧٢ cm^{-1}, while the peak at ٨٢٠ cm^{-1} is linked to C-H bending in disubstituted (para) aromatic compounds and the peak at ١١٠٥ cm^{-1} to C-O stretching in the C-O-C group. The FTIR peak at ١٢٢٦ cm^{-1} corresponds to C-O stretching in C=C-O-C, while peaks at ١٣٦٧ and ٣٣٢٦ cm^{-1} reflect phenolic OH bending and stretching, respectively. The FTIR peaks at ٢٨٧١ and ٢٩٦٤ cm^{-1} correspond to the asymmetric and symmetric stretching of methyl C-H, while the peak at ١٤٤٦ cm^{-1} confirms both C-H asymmetric and symmetric bending, as well as methylene C-H bending. The peak at ٢٩١٩ cm^{-1} represents the asymmetric and symmetric stretching of methylene C-H, while the peaks at ١٥٠٧ and ٢٨٧١ cm^{-1} confirm C=C-C aromatic stretching and C-H stretching in the methylene group, respectively. The peak at ٣٠٢٦ cm^{-1} is indicative of terminal (vinyl) C-H stretching and Ar-H stretching.

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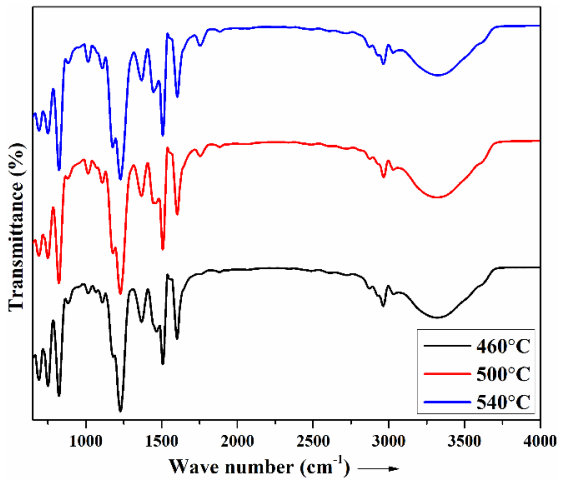


Figure ٧: FTIR analysis of pyrolytic oils from PC at varying temperatures

Earlier studies also support the functional-group assignments observed in the present pyrolytic oils. Apaydin-Varol et al. reported aromatic/aliphatic hydrocarbons and O–H-containing products during polycarbonate pyrolysis, supporting the assignment of the corresponding C–H and O–H vibrations observed in the present study [١٠]. Antonakou et al. reported FTIR characteristics of polycarbonate-containing waste, including substituted aromatic rings, CH_3 groups, and carbonyl functionalities, which are consistent with the corresponding bands observed in the present study [٢١]. Jang and Wilkie reported phenolic, aromatic, aliphatic, alcohol, and carbonate-containing species among the thermal degradation products of polycarbonate, further supporting the functional-group assignments observed in the present study [١٢].

٤. Conclusion

The thermal degradation behavior of waste polycarbonate was systematically investigated under both isothermal and non-isothermal conditions using model-fitting, model-free, and batch pyrolysis approaches. A maximum weight loss of ٨١٪ was observed under non-isothermal conditions at a heating rate of ٥ °C/min, whereas a maximum weight loss of ٨٣,٥٪ was achieved under isothermal conditions at ٥٤٠ °C. The non-isothermal and isothermal degradation processes followed the F٣ and F١ reaction mechanisms, with activation energies of ١٤٢ kJ/mol and ٣٢,٤٤٤ kJ/mol, respectively. The kinetic triplets were optimized in this work. These optimized kinetic triplets are applied to design a suitable reactor for commercial valorisation of the discarded polycarbonate. The batch pyrolysis of the discarded polycarbonate generates valuable plastic fuel oil which can substitute for fossil fuel oil. The pyrolysis conditions were also optimized in this work. These optimized pyrolysis conditions are applied to make a standard optimized pyrolysis process for commercial valorisation of the discarded polycarbonate. The GC-MS and FTIR analyses confirm the presence of different compounds of alkanes, alkenes, alicyclic compounds, aromatic hydrocarbons, and oxygenated compounds in pyrolytic oil, which can be used for the extraction of different valuable chemical compounds. Overall, the optimized conditions and standard pyrolysis process are a promising and sustainable approach for the recycling of the waste polycarbonate and alternative energy recovery, and chemical recovery, causes the promotion of circular economy practices. However, further research is needed to update and validate this optimized pyrolytic process

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and design a suitable reactor that provides economic benefits, creates plastic waste-free, sustainable environments, and offers an alternative way to address the energy crisis by substituting plastic oil.

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