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Application of computational approach in plastic pyrolysis kinetic modelling: a review

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Abstract

During the past decade, pyrolysis routes have been identified as one of the most promising solutions for plastic waste management. However, the industrial adoption of such technologies has been limited and several unresolved blind spots hamper the commercial application of pyrolysis. Despite many years and efforts to explain pyrolysis models based on global kinetic approaches, recent advances in computational modelling such as machine learning and quantum mechanics offer new insights. For example, the kinetic and mechanistic information about plastic pyrolysis reactions necessary for scaling up processes is unravelling. This selective literature review reveals some of the foundational knowledge and accurate views on the reaction pathways, product yields, and other features of pyrolysis created by these new tools. Pyrolysis routes mapped by machine learning and quantum mechanics will gain more relevance in the coming years, especially studies that combine computational models with different time and scale resolutions governed by "first principles." Existing research suggests that, as machine learning is further coupled to quantum mechanics, scientists and engineers will better predict products, yields, and compositions, as well as more complicated features such as ideal reactor design.

Introduction

Modernity has been undoubtedly supported by the progress of plastic materials. As a result, plastic is ever-present in applications ranging from food packaging to the aerospace industry. However, exponential consumption patterns and unrepentant

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plastic pollution are negatively impacting our ecosystems. Therefore, several efforts based on primary, secondary, and tertiary technologies have been applied to reduce the effect of plastic waste on the environment [1]. Many European countries, among others, have pursued the "reduce, reuse, and recycle" policy to eliminate the plastic materials that end up in the oceans, rivers, and landfills. However, it is estimated that just 10% of all worldwide plastic waste produced since 1950 has been effectively recycled [2], which indicates more concerted efforts are needed to solve plastic-based pollution globally.

New technologies view plastic waste as a potential feedstock [3]. The literature reviews of Al-Salem et al. [1] and Schwarz et al. [4] show an overview of these technologies and applications. The recent analysis by Rahimi et al. [5] shows that chemical recycling, especially catalytic pyrolysis, might be the most suitable technological solution in plastic recycling strategies. This approach could prevent 3.5 billion barrels of oil from entering the plastic loop, thus saving around US$ 38 million annually.

The general concept of plastic pyrolysis involves the breakdown of the polymer into smaller molecular fragments that can be used as a value-added commodity or building blocks for the production of fuels, polymers, and carbon-based materials including carbon nanotubes and graphene [6]. Plastic pyrolysis leads to the formation of oil, gases, and solid char, which are closely dependent on the operational parameters, including the feedstock employed. Despite the great advancement of pyrolysis technologies, some technical and fundamental bottlenecks need to be addressed before the process is viable at the commercial scale. A recent analysis by the United States Department of Energy (US-DoE) shows knowledge gaps in catalysts designs, processes, and material feedstocks that need to be overcome in the coming years to enable plastic circularity [7].

To fill such gaps requires polymer pyrolysis modelling, which is the process of defining, categorizing, mapping multiple chemical reactions, feedstocks and products. Models provide insights into how particular polymers are transformed into smaller molecules and then reassembled into new materials. This kind of modelling involves data on broad kinetic processes and detailed data on specific, sometimes microscopic reactions.

This approach involves sequential multiscale modelling from micro- to macro-scale reactor levels, along with solid–liquid–gas phase interactions [8]. However, transforming discarded plastics into higher-value products also requires more accurate determination of the thermodynamic parameters of the depolymerization reactions. While polymer synthesis is an exothermic and relatively simple reaction dominated by the C–C bond formation, the opposite reaction, depolymerization, is an endothermic process. The energy-intensive characteristic of such processes makes it difficult to selectively break down the C–C bonds and achieve high yields of the desired products without also generating undesired radicals or highly reactive molecules that produce other unwanted products. Therefore, there is no universal or multi-purpose catalyst for all plastics, which means it is necessary to select the catalyst according to the polymers and the desired target of products needed.

Most of the research carried out at lab scale [9] and bench-scale [10] has shown the potential of zeolites [11] and transition-metal catalysts to convert raw plastic

materials into fuel or other commodities [12]. However, when real waste is used, the results obtained differ from the yield and composition of the products obtained or predicted from the pyrolysis of the virgin polymer. On one hand, such gaps happen because real waste shows a broad composition of plastic material with different properties including additives along with a small number of metals and other impurities, which have great impact on the reaction performance. On the other hand, the global kinetic expression typically used to analyze the kinetic information fails to capture and drive the complex and interlinked nature of these reactions [13]. Such limitations have hindered the growth and development of plastic pyrolysis technologies. However, the deep details about the progress and evolution of pyrolysis technologies is reported in the literature [14].

To address these gaps, "data-driven" tools, based on machine learning (ML) and quantum mechanics (QM) have been widely applied to unravel reaction mechanisms and kinetics triplets [15–19]. For this reason, the following sections of this review explore the recent advances of computational tools, such as ML and QM, applied to obtain kinetics and mechanisms information of plastic pyrolysis. First, a recent literature review of the general methods and limitations of the kinetic models is provided, followed by an analysis on the progress of ML tools in plastic pyrolysis modelling. Finally, a new perspective combining fundamental knowledge based on QM and previous modelling tools to overcome barriers in the plastic pyrolysis field is described. To the best of our knowledge, this is the first work that summarizes the recent state-of-art research works for the application of ML and QM in the pyrolysis of plastics.

Methods

The Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) method was adopted in this study. The methodology requires four systematic steps: (i) identification; (ii) screening; (iii) eligibility; and (iv) qualitative synthesis. These steps are summarized in Fig. 1. Based on the previous review on plastic pyrolysis [20], the identification process in this study focused on publications (articles, proceedings and reviews) in the Web of Science (WoS) and Scopus databases. The final search was performed on 30 March 2021 and the time frame was set at 2001–2021. In both queries, the search string used consisted of the following search terms and Boolean operators: ("plastic waste" OR "polymer waste" or polyolefin* or polyethylene or polypropylene or polystyrene or "polyvinyl chloride" or "poly(ethylene terephthalate)") AND ("thermal pyrolysis" or "catalytic pyrolysis" or "thermal cracking" or "catalytic cracking" or "thermolysis" or "thermocatalytic"). The first query included a third operator and group of search terms: AND (("machine learning" OR "neural network" OR "ANN" OR "pattern recognition" OR "Statistical Inference" OR "structured prediction" OR "ensemble algorithm*" OR "big data")). The second query used the AND (("DFT" OR "Density Functional Theory" OR "ab-initio" OR "VASP" OR "Molecular Dynamics" OR "Quantum Mechanic" OR "ReaxFF")). The two queries resulted in 2816 documents, of which 729 were removed as duplicates. Next, an initial screening process was conducted,
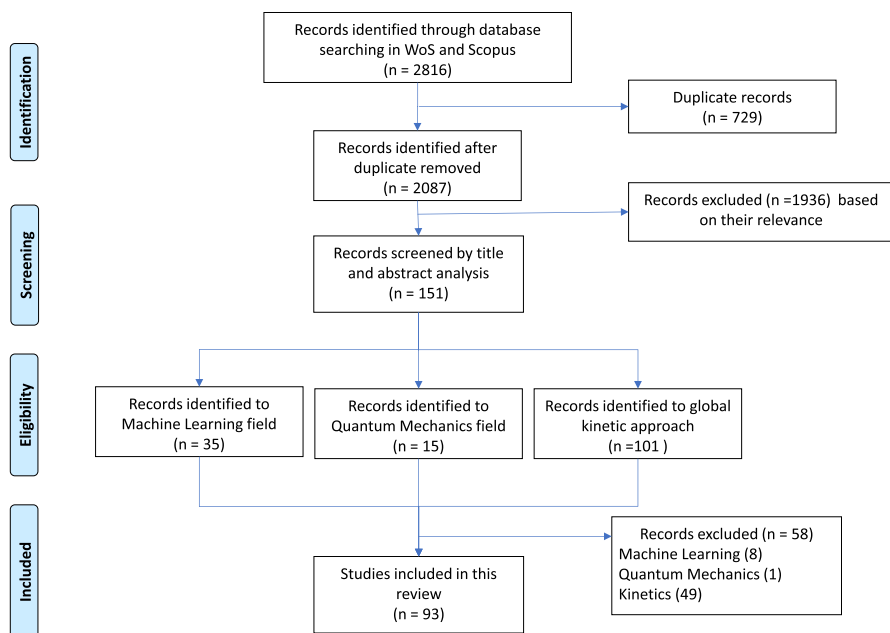
Fig. 1 Flow diagram illustrating literature research and selection process based on PRISMA model (Adapted from Moher et al.[21])

which involved scanning titles, keywords, and, when appropriate, the abstracts to locate the relevant articles. The articles that focused on theoretical approaches, case studies, or others not directly concerned with the kinetic parameters of pyrolysis were removed from the dataset. During this stage, 1936 articles were removed. This was followed by a second screening process, based on a more detailed analysis of the abstracts (151 remaining articles), which was performed and separated based on their primary subject. The final dataset contained 93 documents, which were then used to synthesize this review.

Global kinetic models

Thermochemical routes, including pyrolysis, offer promising methods to reduce plastic pollution. Among the different thermo-degradation routes, the catalytic pathway has the potential to (i) reduce the reaction temperature, and (ii) achieve the desired and narrowed distribution of products [22]. From an engineering point of view, the optimization of the plastic conversion and yields of desired products requires attention to many interlinked parameters.

Global kinetic modelling, in comparison to semi-detailed approaches, implies the selection of a few critical reactions from the hundreds of species and thousands of reactions that may occur during chemical transformation. This simplification of

the reaction networks entails a loss of mechanism information leading to inaccurate data-fitting and conclusions.

For instance, the most common control parameters from global kinetic modelling in pyrolysis are temperature, heating rate [23, 24], pressure [25], catalyst [26], feedstock composition [27], and reactor configuration [28]. Despite the numerous detailed experiments, consensus about which parameters have more impact on the conversion and product yields and the corresponding kinetic models is lacking. Kinetic modelling has allowed engineers to accurately predict the product distribution and kinetic parameters e.g. in synthesis or decomposition of ammonia [29]. However, the kinetic modelling of plastic waste conversion particularly for the catalytic route remains limited because the nature of these reactions is not well understood [30].

Based on the recommendation of the Kinetics Committee of the International Confederation of Thermal Analysis and Calorimetry (ICTAC) [31], researchers extensively explored the kinetic parameters of plastic pyrolysis using various model methods. For example, the model-free methods of Friedman, Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO), or the model-fitting methods of Coats-Redfern have been examined in the past two decades. However, some gaps remain around the process that involves multiple-step kinetics such as determining the kinetic triplets from real plastic waste, which is the main goal, and the crucial step in the scaling-up process [17, 32, 33]. A deep analysis of triplet where multiple-step kinetics such as those involved in plastic waste pyrolysis, requires evaluation through nonlinear methods that involve more complex analysis and data processing [34–36].

Different approximation methods have been developed to evaluate the activation energy (E_a) and the rate-determining step (or mechanism) in plastic pyrolysis, based on thermogravimetric analyses, which are well discussed by Liu et al. [37] and Wang et al. [38]. However, the kinetic parameters obtained do not represent the intrinsic kinetic values of the reaction per se. Hence, the data are commonly expressed as apparent activation energy and apparent pre-exponential factor [39]. This difference also highlights the poor suitability of nth order reaction models. Experiments using iso-conversational approaches have obtained distinct kinetic conclusions despite using the same feedstock and similar thermogravimetric analysis [40].

Urionabarrenechea-Lopez et al. [41] used an empirical model to predict the product yields from real municipal plastic waste, which could be considered as the "holy grail" for the waste-to-valued-added products. The authors found highly acceptable results, reporting a difference between model results and real data of 2–5%. Although satisfactory but "time-saving", these models are too simplistic and cannot predict specific compounds, which is a key aspect of using pyrolysis as waste-to-fuel or waste-to-energy routes.

The discrepancies in global kinetic models are exacerbated by catalytic processes. These simplifications occur due to catalyst deactivation, mass, or heat transfer limitation phenomena, which significantly affect the reaction pathways and product yields. In summary, the models tend to overlook the physical and chemical backgrounds of the underlying chemical reactions [42]. As described above, the kinetic analysis of plastic pyrolysis is a complex task, and different models reflect relatively

narrow parameters or experimental conditions, including feedstock. Although this approach has provided a useful overview of the kinetics and mechanism of plastic pyrolysis, it is limited in length and time scale, which explains the need for new approaches.

Table 1 summarizes the kinetic parameters recently reported for different plastic feedstock for pyrolysis. The list includes Polypropylene (PP), Polyethylene (PE), Polystyrene (PS), High-Density Polyethylene (HDPE), Low-Density Polyethylene (LDPE), Polybutylene Terephthalate (PBT), and Acrylonitrile Butadiene Styrene (ABS). The different kinetic methods (previously mentioned), including the power-law and Sestak-Berggren models, have been compared. Significant differences regarding the kinetic parameters can be highlighted, even when the same materials are analyzed by different methods. The observation hampers consensus about the dominant reaction mechanism, which makes it quite challenging to select the best way to produce a certain kind of product.

To overcome such limitations, Lin et al. [50] proposed the use of the lumping-kinetic (LK) model that divides the entire process into several steps and measures different "categories" of simplified reactions between the lumps. Normally these lumps are also called pseudo-components or "families," and are surrounded by chemical compounds according to intrinsic properties such as boiling point. In the work carried out by Lin, the lumps are portioned into three major fractions according to the average number of carbon compounds. The results showed that LK-modelling presents a feasible option for reducing the complexity of the underlying chemical network. However, this strategy proves inadequate for predicting the entire reactor composition, especially when different feedstock compositions are used in the same lumping and the physicochemical nature of the reactions cannot be anticipated.

Other approaches based on the immiscibility of pyrolysis products (liquid, gas, and char) and binary activity coefficients have been used by Fakhrhoseini et al. [42] to estimate the product yields. When model results are compared with the real yields obtained from the individual and different mixtures of plastic feedstock, it appears that the overall process can be modelled. Yet, substantial differences in the composition of products limit the application of such approach.

Although the aforementioned approaches may provide necessary and useful snapshots of pyrolysis, scientists cannot still track all the reactions. Therefore, this results in overestimated parameters (activation energy, pre-exponential factor, and kinetic order), which are only valid for a narrow set of conditions.

Semi-detailed kinetic models

Kinetic models based on single-step mechanisms are more accurate, but the feasibility of such models is dependent on the number of reactions involved, thus it is expensive and time-consuming. For plastic pyrolysis, this network involves hundreds of chemical compounds and thousands of chemical reactions, which increase exponentially with the number of carbon atoms involved. The recent work by Dogu et al. [17] details the strengths and limitations of different kinetic approaches for the pyrolysis and gasification of plastics. In addition, Dogu

Table 1 Representative kinetic parameters calculated by different global-based models for plastic pyrolysis reaction

Plastic	Kinetic parameters			Selected method	References
	Activation energy, Ea (kJ/mol)	Reaction order, n	LnA, (s^{-1})		
HDPE	256	0.50	–	Friedman	Aboulkas et al. [43]
PP	189	0.50	–		
PBT	176	0.92	25.42	Sestak-Berggren	Sánchez-Jiménez et al. [44]
	180	1.13	26.52		
HDPE	227 / 80	1	34.94/11.91	Coast-Redfern	Costa et al. [45]
TV-shell (PS-ABS)	184–278	–	28.2–45.3	Friedman	Yao et al.[34]
	184–269	–	27.1–42.7	FWO	
	157–337	–	19.7–54.1	KAS	
PE	252	–	–	Friedman	Pan et al. [46]
	241	0.85	34.5	Genetic-algorithm+reaction-order	
Waste milk package	139	–	26.7	KAS	Saha et al. [47]
	143	–	26.8	FWO	
HDPE	194	–	–	KAS	Al-Yaari et al.[48]
	186	–	–	Friedman	
LDPE	193	–	30.3	KAS	Dubdub et al. [49]
	194	–	31.5	Friedman	

– Not available

highlights the relevance of incorporating computational tools to have better and more accurate kinetic models to tackle plastic waste recycling through pyrolysis.

Complicated reaction systems, like plastic pyrolysis or cracking, depend on many kinetic parameters. Some efforts to retrieve precise information about kinetic parameters have been pursued by Levine et al. [32], who employed the method of moments approach that combines the theory of reaction with balance-based models. By solving moment equations, the authors can follow the evolution of the molar mass distribution of the products. The authors used the global rate coefficients considering zero, first, and second moments to satisfactorily describe the changes in the molecular weight distribution as a function of time. The method proposed detailed mechanistic models for polymer reaction systems to track 151 species and 11,000 reactions from single polyethylene pyrolysis. Despite the study's enhanced understanding of the reaction pathway, the findings should not be interpreted as definitive because end-chain radicals can be formed by multiple pathways that can affect the overall yield of HDPE decomposition. These results could be improved by distinguishing the reactions pathway and product formation based on information retrieved from advanced characterization techniques.

Recently, the foundation of the chemical and physical processes involved in the pyrolysis of polymers has been addressed by experimentation based on diffuse reflectance spectroscopy of cellulose [51], and a new thermal-pulsing reactor for pulse-heated analysis of solid reactions [52]. Both techniques provide further details on the kinetics and mechanisms of polymer decomposition. Although biomass conversion is the primary goal of the research, fundamental knowledge retrieved from these investigations highlights the molecular and short-time scales in plastic pyrolysis. Linking the atomic scale with the unravelling cleavage and bond-formation to the mesoscale level, where inter- and intra-molecular forces impact the final macroscale properties will uncover new strategies based on high-throughput experiments and computational modelling tools. Such differences have been highlighted in previous work by Sánchez-Jimenez et al. [39]. The authors show that model-fitting methods are "less time consuming" when used to study the kinetic modelling of plastic pyrolysis, but these models do not reveal the real evolution of the reactions. Based on the arguments described above, the highly complex nature of plastic pyrolysis is the main obstacle for scientists to accurately describe and predict the real process using kinetic modelling. However, the large amount of experimental data indicates a new paradigm in chemical engineering organized by computational tools including artificial intelligence (AI).

Concerning this matter, more detailed knowledge about the kinetic and mechanism in real-time based on predictive science-based models is required, as the US-DoE has identified in their report, "PRO 4: Develop Novel Tools to Discover and Control Chemical Mechanism for Macromolecular Transformation"[7]. In this regard, the following section explores the most recent efforts and progress supported by different computational tools like AI to unravel key aspects related to the kinetics and mechanism of plastic pyrolysis.

Insights from "in silico" modelling

Traditionally, heterogeneous catalysis progresses through abundant experimentation, trial-and-error discoveries [53], and a systematic approach using model catalysts, molecules, and physics-based modelling [54]. One of the most famous examples regarding the experimentation-based approach is the progress made over ammonia synthesis catalyst by Haber and then by Mittasch and Bosch in the first decades of the twentieth century [55]. The final progress and understanding of this reaction were achieved after 10,000 experiments during which different single- and multi-combination of metals led to the final Fe-based catalyst [56]. The application of computational tools based on AI strategies can reduce the time and investment required to synthesize, test, and increase the efficiency of these processes [57, 58].

The application of AI to chemical engineering disciplines such as catalysis, material science, energy, and fuels has gained significant attention in recent years [18, 59, 60]. The progress of ML in chemical processes has been explicitly described by Venkatasubramanian [61], as summarized in Fig. 2 showing the most relevant milestones achieved during the last 50 years. The authors categorize the evolution of ML in four phases or stages, according to the improvement of the technology and computational task force. Moreover, the authors opine that one of the most important challenges that scientists are facing is the development of fundamental knowledge based on a mathematical framework. The proposed framework should predict macroscopic properties from various fundamental "first-principles" and mechanisms, which cannot be achieved using global kinetic or physics-based models alone.

In 2018, the first Turing test for chemical synthesis resulted in a machine that discovered a more effective retrosynthesis route for small organic molecules than those proposed by scientists [62]. Other influential works addressed by computer-generated reaction predictions and automated technicians (robots) have shown to be more accurate and involving less time than those performed by humans [63, 64]. The fast and accurate development of in-silico tools based on ML for various chemistry fields and processes will increase in the coming years. An analysis of this trend was recently reported by García [65]. The next section will highlights the impacts of the new approaches on pyrolysis research.
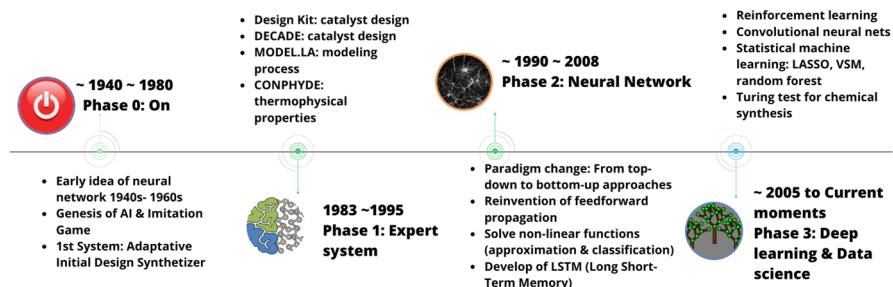

Fig. 2 Major timeline evolution of computational tools based on ML for chemical engineering applications

Machine learning for plastic pyrolysis

In-depth investigations on the kinetic parameters and mechanisms for plastics pyrolysis are complicated due to the numerous interlinked network reactions that occur simultaneously. Hence, the prediction of product yields and reactor modelling is extremely complex [66]. Based on the documents dataset examined, the landscape of plastic pyrolysis is being transformed by ML-based tools such as artificial neural network (ANN) [67], genetic-algorithm-artificial-neural-network (GA-ANN) [46], and support vector machines (VSM) [68].

Although the ultimate goals are similar, the tuning capabilities of global kinetic models and the capability of machine learning are quite distinct. In global approaches, the starting parameters must be provided from previous research or based on general assumptions (isothermal conversion, non-transfer mass balance, and energy limitation, etc.). However, in machine learning, the starting parameters are discovered during the training of the algorithms to learn the data structure without previous considerations.

In general, ANN organizes data, "learns" to recognize patterns, and then predicts the outputs for a new set of similar data. An ANN consists of neuron layers with less than two hidden layers, which is the core processing unit of the network. A neural network with more than 2 hidden layers is considered a deep neural network [69]. ANN is constituted by (i) an input layer, which receives the input data; (ii) an output layer predicts results; and (iii) a hidden layer, which is located between the input and output layers performing most of the operations required by the network (see Fig. 3). The details of the underlying algorithms, architecture
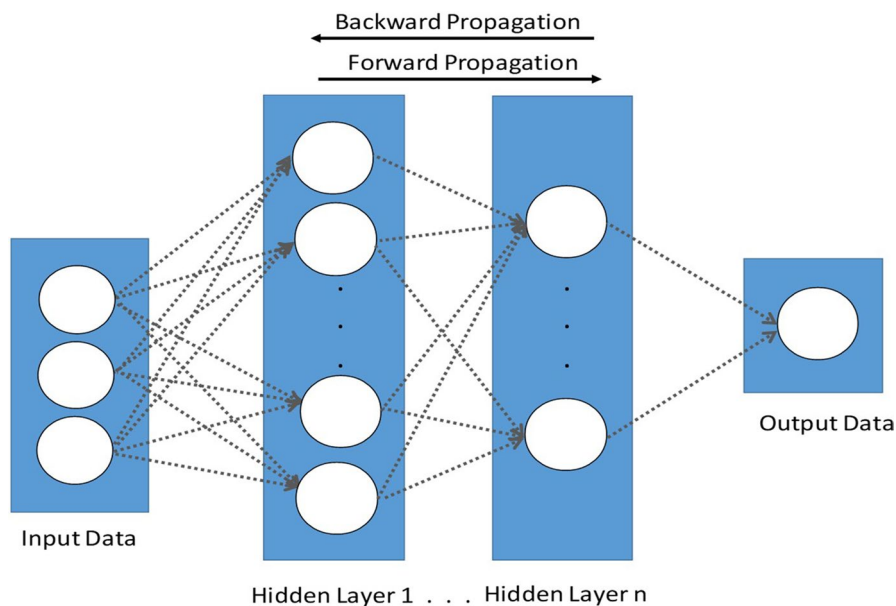

Fig. 3 Schematic representation of a typical artificial neural network (ANN)

together with the "forward" and "backward" propagation techniques used to train the networks are extensively reviewed in the literature [70–72].

The adoption of ML and its representative subset in chemical engineering and other subfields has increased in a sustained way in the last decade and have been addressed by Tkatchenko and Dobbelaere [18, 73]. One of the major areas with notable progress in this field is "in silico" catalyst synthesis, drugs, and materials design, among others [74, 75]. New applications to understand the relationship between catalyst properties versus reaction performance are increasing rapidly.

For decades, "chemical intuitions" have driven scientists to formulate mathematical equations to describe chemical phenomena. However, attempts to describe them in this way relies heavily on simplifying assumptions, which sometimes do not represent the real reaction networks. Nevertheless, the current evolution of ML has increased the ability to screen different reaction pathways with non-linear relationships and overcome traditional bottlenecks shown by the "chemical intuition". The recent application of ML in plastic pyrolysis signifies a new and more computationally feasible approach to predict reaction yields, mechanisms, and kinetic parameters. The outlined aspects are fundamental to scaling-up processes, especially those that cannot be tracked using traditional kinetic models.

The application of ML in plastic pyrolysis has been demonstrated by Conesa et al. [76]. This study represents one of the first attempts to train ANN to investigate the kinetic parameters of the thermal degradation of PE and other natural polymers. By selecting 20 points from each of the experimental TGA curves at different heating rates, as input data, and 20 neurons in the input, 10 neurons in the hidden layer, and 3 neurons in the output layer (ANN-20-10-3), the authors were able to predict accurately the kinetic parameters (activation energy Ea, reaction order n, and the pre-exponential factor k_0) in the range reported in previous works by model-free or model-fitting approaches.

Similarly, Fazilat et al. [77] obtained good accuracy in determining the kinetic parameters for the thermal degradation of Nylon 6 (or polycaprolactam). This was achieved by incorporating ANN and adaptive networks based on fuzzy interference systems to reveal the nature of the relations made by the ANN. Despite the lack of information on the number of neuron layers, this work represents a milestone on the application of ANN to plastic pyrolysis. The modelling tool used by the authors generated results that were quite close to the experimental data and the Friedman or the KAS model. The findings signify the possibility of integrating the predictive models and decision-making tools in the plastic pyrolysis process.

Abnisa et al. [78] employed ANN to estimate the composition yield for the pyrolysis of plastic wastes such as HDPE, LDPE, PP, and PS in a fixed bed reactor. Furthermore, the authors used a combination of plastic waste and pyrolysis products as input and output data for training the ANN. Based on an ANN architecture of four neurons for the input layer, ten in the hidden layer, and the other three for the output layer (ANN-4-10-3), the authors successfully and precisely predicted the experimental and reported data with a very low mean square error ($MSE < 2.6 \times 10^{-4}$) and a high coefficient of determination ($R^2 > 0.9$). However, the work of Abnisa was based on architecture similar to the version used by Conesa [76]. The authors used

data obtained from a batch reactor, which is a more reliable scale than applied in previous studies conducted by thermogravimetric analysis.

Al-Yaari et al. compared the effects of different neural network architecture and transfer functions to develop a highly efficient kinetic model for LDPE pyrolysis [48, 49]. The findings reported in the two publications strongly agree with the calculated values from the global kinetic model (see Table 1). The results confirm the versatility of the ANN, which is based on two different architectures (ANN-2-10-10-1 or ANN 3-10-10-1) and the capacity of the two transfer functions (Tansig-Logsig or Logsig-Logsig) to model the catalytic pyrolysis reaction of LDPE and HDPE, respectively. While the authors did not conclude in favor of a specific approach, based on the MSE and R^2 obtained, the ANN-3-10-10-1 and Logsig–Logsig are the best architecture and transfer functions, respectively. The results provide further indication that ML applications are effective in terms of MSE and R^2. This study suggests that the best configurations for plastic pyrolysis, according to the literature presented here, are one or two hidden layers with 10 neurons in each hidden layer, which is in good agreement with the results reported by Conesa [76] and Abnisa [78]. Nevertheless, determining the number of neurons or hidden layers for data modelling requires trial and error. Stathakis encourages the use of a genetic algorithm [79], nevertheless, this is only a general idea, and neuron layers must be moulded based on specific parameters as demonstrated by Al-Yaari [48].

With the increasing machine power, new approaches that focus on the mechanics of natural selection and natural genetics such as GA-ANN have been employed to analyse and optimize the kinetic triplets of plastic pyrolysis reactions. Both ANN and GA-ANN aim to achieve the best results possible albeit in different ways. Although ANN is used to predict the solution for the given inputs, genetic algorithms are strongly focused on the optimization of the problem. Several applications based on genetic algorithms have shown their applicability in chemical engineering [80] and biotechnology [81], among other fields.

Saha et al. [82], employed a genetic algorithm to evaluate fifteen different decomposition models reported in the literature. The advancement of this work relies on two aspects: (i) support for the ANN on genetic algorithm, and (ii) application of ML to model the data obtained from catalytic pyrolysis reaction of PP (based on Al-MCM41). From the analysis, the authors suggested that the degradation of PP changes from initiation-propagation to random scission mechanism after the weak links are consumed. In this line, similar results have been reported by Reddy et al. [83] for PP pyrolysis using HZSM-5 as a catalyst by exploring parallel approaches based on genetic algorithms (GA). Comparing this work to the previous one, it is possible to note that GA can predict variations of the kinetic parameters according to the catalyst used (128 kJ/mol vs 92 kJ/mol for Al-MCM41 and HZSM-5, respectively). Despite the accuracy obtained by implementing the GA for simultaneously comparing different kinetic models, the strong similarity between the models makes it necessary to analyze and track the reaction with other tools such as "operando" to reveal the precise decomposition model and the rate-limiting step. Other recent analyses on virgin plastics such as polystyrene and polyurethane [84] or plastic waste [46] using GA have been highlighted with a high degree of confidence. Istadi et al. [85] showed that hybrid GA-ANN can predict the evolution of liquid yields

during the catalytic conversion of PP/PE. The authors optimized the reactor conditions to achieve the maximum yield of C_4–C_{13} liquids with relatively high accuracy. Although this work does not display the computed kinetic parameters, the modelling results demonstrate that catalyst characteristics exert significant effects on product yields.

Understanding and predicting the reactor's behavior is one of the major tasks in the scaling process. Moein et al. [86] examined this issue by testing different types of plastic feedstock to simulate the typical composition of plastic waste. The authors evaluated the capability of the ANN and Least Square Support Vector Machine to predict the gas and liquid products. Based on the reaction temperature, catalyst/feedstock ratio, and reaction time data, the authors simulated the product yields with a high confidence level. The modelling result shows that each design is statistically adequate in terms of R^2 and MSE, making both quite precise and reliable tools.

Machine learning has proven to be suitable for unravelling the kinetic triplets of plastic pyrolysis and highlighting the kinetic mechanisms involved. However, the data-driven models must be supplemented by critical analysis of the physicochemical phenomena behind a chemical reaction such as the breaking and forming of bonds. Data-science tools such as ML can offer "black-box" solutions constructed upon the relationship between input data (mass loss) and the output data (activation energy). This does not capture the chemical process in the same way as a physics-based model in which mathematical equations are built upon data developed by measurements of intrinsic phenomena such as surface adsorption, bonds formations, and conversion among others. Our review suggests that the future of ML for predicting and unravelling the physicochemical nature of processes should be based upon "first-principle knowledge," which is similar to quantum mechanics. Some spark in this direction is highlighted in the next sections.

Quantum mechanics for plastic pyrolysis

Several tools based on QM, such as ab initio, molecular dynamics (MD) or density functional theory (DFT), have led to a deeper understanding of the microscopic relationship between atoms. These types of computational tools are based on solving the molecular Schrödinger equation and the electronic density function for ab initio and DFT, respectively [87]. Since electrons movements are governed by the laws of quantum mechanics, the many-electron problem is, in principle, fully described by a Schrödinger equation. However, the electrostatic forces between the electrons make its numerical resolution an impossible task in practice, even for a relatively small number of particles or ideal systems. While the analysis of the DFT theory is not the aim of this review, the article, "A Primer in Density Functional Theory" [88] offers a good starting point on this topic. DFT is one of the most common approaches to quantum simulations. DFT establishes that all the properties of the ground state of a system are a function of their charge density, which requires complex and computationally intensive tasks. Hence, the kinetic modelling and estimation of product yields based on QM-level calculations require significant computational power. This is particularly evident when calculating the representation of large molecules and

their interactions during a chemical reaction. However, these models have recently grown in popularity due to the development of user-friendly software packages.

A potential class of catalysts, known as alloy nanoparticles, offers another particularly interesting application of QM coupled to ML for fields such as fuel cells, biomass conversion, and natural gas conversion [89]. The drawback may be the requirement of exascale computing power and highly efficient optimization algorithms for the ML component, although such methods are still under development. Despite the advancements of QM tools, DFT remains limited by (i) the delocalization error of approximate functional, and (ii) the static correlation error of approximate functional [16, 90]. These errors limit the ability to properly estimate the barriers of the chemical reactions and fail to describe, degenerate or near-degenerate states during the breaking and formation of chemical bonds. Cohen et al. [90] and Schleder et al. [16] present a deeper and detailed explanation of the current limitations and state of DFT.

The most successful models that describe the reaction at the atomic level are created with tools such as Reactive Force-Field Molecular Dynamics (ReaxFF) [91]. ReaxFF can describe reactive systems in large-scale dimensions with the accuracy of QM, but with lower computational efforts. These tools could provide deeper insights to the researchers on the mechanisms and product yields of the degradation process of complex molecules under reactive environments, such as non-catalytic plastic pyrolysis.

Kinetic and mechanistic information provide part of the fundamental knowledge necessary to achieve future scalability of plastic-to-fuel processes. In this sense, Liu et al. [92] analyzed the evolution of pyrolysis products by ReaxFF simulations, and their results showed a detailed mechanism for the majority of products formed at different temperatures by coupling the modelling with Visualization and Analysis of Reactive Molecular Dynamics (VARMD). These computational approximations were able to illustrate a highly complex chemical reaction network, emphasizing the most important reaction pathways. The results obtained from the kinetic analysis are detailed in Table 2, which is also consistent with other work in this field [93].

Table 2 Representative kinetic parameters calculated by different quantum mechanics tools for plastic pyrolysis reaction

Plastic	Kinetic Parameters			Modelling	References
	E_a (kJ/mol)	Reaction order, n	LnA, (s^{-1})		
Sulfonated-PE	200–210	–	–	ReaxFF + Kinetic-Monte Carlo	Younker et al. [97]
HDPE	250–258	1.50	21.8–25.2	ReaxFF + VAR-MD	Liu et al. [92]
PE	230–280	0.87	13.0	ReaxFF	Liao et al. [94]
PI	187	1	35.2	ReaxFF	Lu et al. [98]
PE	403–439	0.62	40.4–40.5	ReaxFF	Lane et al. [96]
PE	452	1	–	ReaxFF	Hong et al. [99]
PS	314	1	–		

– Not available

These significant insights present a better understanding required to tune the reaction parameters and implement plastic-to-fuel technologies.

Liao et al. [94] investigated the evolution of the kinetic parameters for thermal decomposition of PE by ReaxFF simulation. The authors followed the evolutions of the kinetic parameters and products. Table 2 shows that the kinetic parameter evolution is correlated with the presence of oxygen during the thermal degradation of the polymer. The simulation captured the temporal evolution of species produced by PE pyrolysis with high accuracy. However, the calculated kinetic parameters indicate that the major mechanism in free-oxygen experiments follows a random scission ($E_a = 230$–280 kJ/mol) in the same order as those published in Table 1, based on global models. The significant variability of E_a reported during low oxygen-concentration experiments (50–400 kJ/mol), could indicate that different mechanisms are taking place according to the evolution of the reaction course.

Decomposition of other types of plastic such as polypropylene (PP), has been followed by molecular dynamics simulation using the AMBER force field package simulator by Huang et al. [95]. The authors showed that during the modelling, three temperature regions can be identified and used to promote the formation of specific compounds: (i) below 550 K, (ii) between 550 and 700 K, and (iii) above 700 K. These three major regions can be associated with: the energy absorption and some changes on C–C bonds length; break down of C–C bonds of the main carbon chain, and finally, the production of small carbon-chain products. The model obtained by the authors showed that thermal decomposition of PP can be carried out by intramolecular hydrogen transfer, and further C–C homolytic cleavage mechanisms. Details about the mechanistic model obtained here can be used to guide researchers to develop better kinetic models or even support physics-based models.

Lane et al. [96] investigated the effect of heating rate by laser-driven experiments of PE thermal degradation by molecular dynamics simulation using ReaxFF. The construction of proper kinetic models for this process focused on determining the effect of the thermal ramp (10^{10}–10^{14} K/s) on the reaction kinetics at 300–5000 K. Due to the experimental conditions, the analysis of the model was carried out in the timescale range of picosecond to nanoseconds. The results obtained from this simulation have been modelled in ultra-high heating rates for a different purpose than plastic pyrolysis, but the kinetic model produced by this approximation showed similar accuracy with the kinetic models based on first-order random-scission which is often used for pyrolysis of PE under ambient conditions [44]. These approximations show the versatility of computational tools for multipurpose analysis.

Outlook on plastic pyrolysis models

Plastic pyrolysis is one of the most suitable tools for plastic waste management. The process can reduce the carbon footprint of plastic and foster the transition to a circular carbon economy. However, some blind spots exist related to the kinetic modelling and reaction mechanisms of plastic waste pyrolysis. The traditional approach based on the kinetic analysis of global models provides scientists with basic knowledge about pyrolysis. These models are limited to narrow ranges of reaction parameters,

dismissing effects of heat and mass transfer as well as catalysts, among other parameters. Such shortcomings explain the need for more detailed kinetic models to predict and track the products of plastic pyrolysis under a wide range of conditions and feedstocks at a high resolution in time and space scales. Obtaining such knowledge can help ease the major bottlenecks and close the loop around plastic waste.

To overcome the limitations of these models, scientists have used ML to develop interatomic potentials and estimate energy interactions. The ML is trained with data generated by QM, which is commonly termed as machine-learned interatomic potentials (MLPs) [70]. These new approaches can be used to explain solid–gas interaction and chemical equilibrium, which could also help to predict the evolution of catalysts under reaction conditions [98]. The progress in this direction has been recently addressed by Jacob et al. [100], and Artith et al. [101].

Recently progress on MLP has been shown by Liu et al. [102] on the pyrolysis of glucose as a probe molecule. Based on global neural network potential, the authors achieved a deep exploration of the evolution of glucose decomposition. After managing 1.2 million minima and 150,000 reaction pairs, the final reaction database was depurated to obtain 4000 unique molecules and 6000 reaction pairs. The results reported by the authors unravelled the most important pathways described for the formation of 5-hydroxymethylfurfural (HMF). The HMF product is the most valuable product observed during experimentation, concluding that the MLP coupled to the global neural network provides a strong tool to explore the complex pathways of chemical reactions.

In plastic pyrolysis, the ML and QM could be useful to predict kinetic parameters and degenerated-state or transition-state energy levels. Although this "strange couple" may sound like science fiction, this partnership is growing and should lead to important breakthroughs in the coming years [103]. Recently, a multidisciplinary team involving the Technical University of Berlin, the University of Warwick, and the University of Luxemburg have developed an ML method to predict molecular wave function and electronic properties of molecules. The tool also captures the degree of freedom in molecules, which is the heart of quantum chemistry and provides access to the chemical interpretation of reactions, bond order, and charge density without any additional ML models for each property [104].

Unravelling and improving the capability to predict new stables structures or potential reaction pathways to achieve desirable products is one of the key points of computational chemistry. Nevertheless, it is necessary to have a deep and detailed understanding about the elementary steps and the abundant intermediate species, which in terms of heterogeneous catalysis means finding the corresponding structure of the transition state (TS). This process is immensely challenging because it involves finding a connection between two lowest-energy paths on the potential energy surface in high-dimensional space. The key here is that ML can accelerate the process of finding the minimum energy paths by acquiring information from quantum data. Although ML and QM for predicting chemical reactions is in a nascent stage, this "strange couple" could be generalized in two ways: Firstly, the focus on ML can learn from quantum chemistry to describe molecular properties (Fig. 4a). Secondly, ML model may predict the ground-state wave function determined by the Schrödinger equation (Fig. 4b). Detailed analysis of these approaches
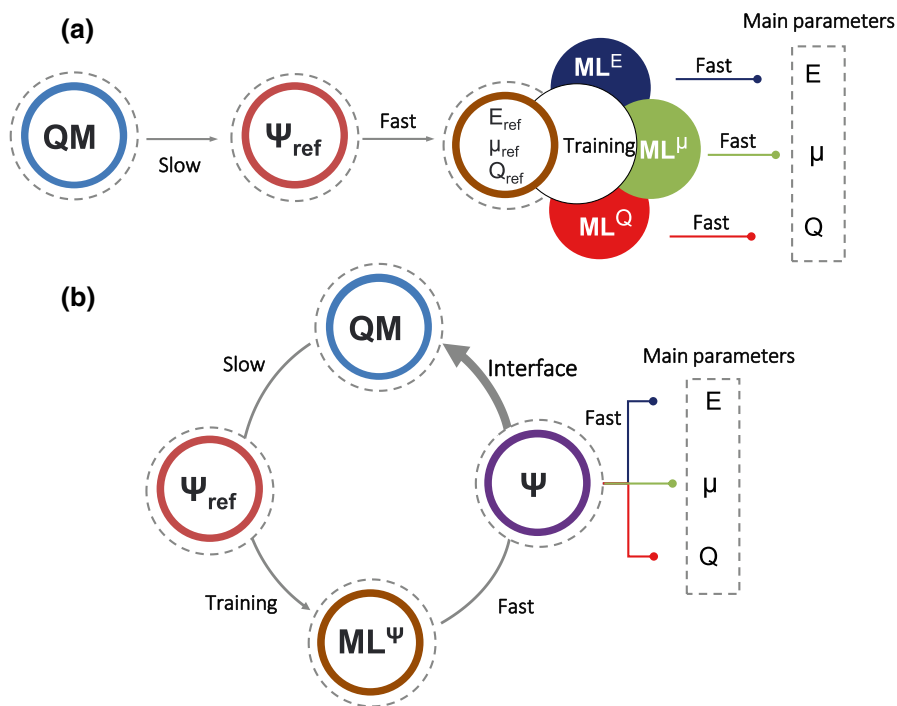
(a)

Main parameters

(b)

Main parameters

Fig. 4 Integration of machine learning and quantum mechanics adapted from [104]. **a** Representative forward ML model. **b** ML predict the wavefunction, which acts as an interface between ML and QM

covers wide-range information that will require expanding the spotlight beyond plastic pyrolysis topics and offering a deep analysis of statics, stochastic and quantum knowledge. However, readers are invited to follow recent and in-depth reviews in this field reported by Noe et al. [105], Rupp [106], and Schutt et al. [104]. These reviews follow the main advantages of integrating different models and how new neural network architectures can improve quantum calculation, especially for reactions involving big molecules.

As noted, most of the works summarized in this paper show that ML or QM present significant advantages to modelling data and obtaining information about kinetic triplets. Still, certain gaps need to be addressed to impact plastic recycling technologies on a global scale significantly. Some of the challenges that can be drawn from this paper include (i) feedstocks main composition: comprehensive analysis of real plastic waste is required to improve the current capability of the artificial networks; (ii) additive and impurities: plastic waste has a high quantity of impurities or other inorganic materials. A detailed analysis of these is quite challenging and theoretically infinite. A starting point could be made by "back-engineering exercises" to understand what the industries do not need. For example, what level of additives or impurities are theoretically permissible during industrial application without causing damage or environmental concerns. Further studies on the impact of bromine, chlorine and other impurities on the

plastic pyrolysis process is required; finally (iii) a "bridge" between ML and QM tools, so that scientists across disciplines can unravel the key aspects for developing proper kinetic models and efficient mapping of the reactors and final products.

Lastly, scientists and engineers will continue to work towards merging ML and QM modelling as a standard tool to improve efficient catalysts prototyping and parameter optimization reactions. New systematic experiments and massive data sets with stronger accuracy, validity and curation techniques will be required for machine learning purposes. The workflow for this "exotic mixture" requires: (i) databases that can hold the prepared-to-use catalysts and operational conditions; (ii) that each catalyst and product must be characterized by its representation (or fingerprint), which consists of its electronic structure and atomic and physical properties (this is where QM plays its role), and (iii) ML will be used to build patterns, discover descriptors, and find models.

Conclusion

Despite the evolution of plastic pyrolysis in recent decades, more accurate and sustainable methods for improving plastics waste recycling are required. In the coming years, research on plastic pyrolysis will make great strides in using ML and/or QM to solve multi-dimensional challenges related to kinetic and timescale modelling. Considering that all properties of a systems, physical and chemical, can be determined by the wave function, the intuitive evolution of this "strange coupling" between ML and QM seems to be focused on find better descriptors and architecture to increase the speed of screening the high number of potential transition state and long-timescale kinetic in high chemical space. This review points out that computational approaches based on ML and QM have the potential to make a strong contribution in the coming years by unravelling complex reaction networks such as plastic waste pyrolysis. This means that new and more scientists have to evolve and adapt their skills to incorporate more "in silico" tools in their daily work.

Declarations

Conflict of interest The authors declare no competing interests.

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