

Muhammad Afzal Raja, Yongsheng Zhao, Xiangping Zhang\*, Chunshan Li and Suojiang Zhang

# Practices for modeling oil shale pyrolysis and kinetics

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**Abstract:** Oil shale is one of the largest, relatively undeveloped natural fossil fuel resources in the world and so an important potential source of energy. The organic matter of oil shale is present as a complex combination of carbon, hydrogen, sulfur and oxygen named kerogen. Pyrolysis-gas chromatography-mass spectroscopy affords the opportunity to chemically characterize the main structural skeleton in this kerogen and is a favorable method to study the structural characteristics of kerogen at a molecular level. The thermal degradation of oil shale kerogen is a complex chemical process, accompanied by the wide variety of products obtained, which poses difficulties in the determination of the kinetics and mechanism of pyrolysis. Understanding the kinetics of kerogen decomposition to oil is critical to design a viable retorting process. Comprehensive kinetic data are also essential for accurate mathematical modeling of various oil shale processes. Classic graphical methods cannot unambiguously measure and estimate kinetic parameters due to the mathematical complexity. Advanced isoconversion methods would be appropriate for the calculation of the distribution of activation energies for multiple reactions involved in the decomposition of complex material such as kerogen to products. The range of variability in the principal activation energy is from about 200 to 242 kJ mol<sup>-1</sup>, with most samples being in the middle half of that range, while the range of frequency factors most likely in the 10<sup>12</sup>–10<sup>16</sup> s<sup>-1</sup> range, with most values within the middle half of that range. The review presents the complexity of the oil shale

pyrolysis mechanism and pyrolysis kinetics along with the challenges in experimental procedures and modeling of oil shale pyrolysis kinetics.

**Keywords:** isoconversion methods; kinetic models; oil shale; pyrolysis; thermal analysis.

## 1 Introduction

Energy demand is one of the most important problems facing the world due to economic and population growth (Yang et al. 2016b). Demand for crude oil, a cheap source of energy, currently making up 34.5% (v/v) of the global energy mix, is expected to grow at 0.8% per annum through 2035 (OPEC 2011, Farouq et al. 2014). The global energy consumption rate made the modern civilization grossly dependent on fossil fuels such as coal, petroleum and natural gas (Maqsood et al. 2014). Exploration of new reserves and evaluation of the potential alternatives have to be considered together to ensure future energy requirements. To pursue the alternative energy sources, oil shale, oil sand, shale gas and coal bed methane have consequently gained worldwide attention (Jinhu et al. 2014, Youhong et al. 2014). Moreover, the uncertainty in petroleum prices and finite oil supplies has motivated many countries to produce and use shale oil as an alternative to traditional petroleum (Ronghua et al. 2014, Xiangxin et al. 2014, Yang et al. 2016a).

The early history of pyrolysis kinetics for natural materials showed a huge variability due to improper experimental design and kinetic analysis methods. Although huge advances in modeling the free-radical chain reactions associated with hydrocarbon (HC) were made in the first half of the 20th century, pyrolysis kinetics of coal and oil shale lagged behind substantially. Over a 20-year period from approximately 1975 to 1995, rapid advancements in equipment and software, driven in large part by advances in modern electronics, provided the methodology to understand the errors of the past and develop reliable methods that could derive chemical kinetics capable of extrapolating from geological time scales of hundreds of millions of years to millisecond time scales of combustion. Much of this advancement in understanding the range of variability in kinetic parameters came from the petroleum exploration geochemistry community, which desired to extrapolate laboratory-based

**\*Corresponding author: Xiangping Zhang,** Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100049, China, e-mail: xpzhang@ipe.ac.cn

**Muhammad Afzal Raja and Yongsheng Zhao:** Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100049, China; and College of Chemical and Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

**Chunshan Li and Suojiang Zhang:** Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100049, China

kinetic parameters over hundreds of degrees and millions of years. The International Confederation of Thermal Analysis and Calorimetry (ICTAC) published recommendations to improve the quality of kinetic parameters derived in the thermal analysis (TA) community. One of the major recommendations is the need for analyzing multiple thermal histories simultaneously, which had been standard practice in the petroleum geochemistry community for decades before. Thus the primary goal of this work is to review the methodologies and practices for kinetic parameter determinations of oil shale. In addition, this work focuses on the challenges in determination of the oil shale pyrolysis mechanism and kinetics, and also concludes with the suggestions and further directions on the way forward.

## 1.1 Oil shale

Oil shales are natural sedimentary rocks. They consist of a mineral porous matrix with the porosity filled with oil, called kerogen, representing 10–65% of the total mass. The mineral matrix consists of carbonates, quartz and clay (Martins et al. 2010). The most important advantages of oil shale over other solid fossil fuels are high H/C atomic ratios in the organic matter, which are as high as 1.7 in some cases (petroleum, 1.9; coal, 0.4–1.0), and a unique organic matter composition, which allows one to obtain a wide range of chemical products, including motor fuels and premium lubricating oils. Figure 1 shows the H/C atomic ratios in various HC materials and final products.

About 25% of the world oil shale production (or 4 mill. t) is processed into shale oil and combustible gas, and then upgraded into jet fuel, gasoline, light fuel oil, bitumen, coke, phenols, liquefied shale gas, wax, lubricating oil and other products (Brendow 2003).

## 1.2 Oil shale pyrolysis and retorting

Oil shale is a petroleum source rock that has not undergone the natural processes required to convert its organic matter to oil and gas. Oil shale has been pyrolyzed to

produce HC oils since the middle of the 19th century (Le et al. 2013). The key to produce oil from these resources is to reduce oil viscosity, and that is best accomplished by heating these resources up to 500°C, which is known as the pyrolysis process (Berna et al. 2008). The organic matter (called kerogen) is less than one third of the shale weight and cannot be extracted by solvent but is easily decomposed by pyrolysis (Khraisha 1998). Among the shale oil recovery technologies, retorting is one of pyrolytic processes designed to produce oil and it is considered as the most effective method for extracting oil from oil shales (Berna et al. 2008, Haifeng et al. 2015). Generally, this process is performed by heating the oil shale inside a vessel called retort in order to promote pyrolysis efficiency (Vahur and Eric 2013). The composition of the products formed during pyrolysis depends on the fundamental chemistry of the organic matter in shale and the reactor configuration as well (Tiwari and Deo 2012a).

## 1.3 Composition and chemical structure of oil shale kerogen

The name “kerogen” was first applied by Crum-Brown in 1912 to denote specifically the insoluble organic matter in oil shale (Rajeshwar et al. 1979, Sun et al. 2015b). The specificity of this definition however was lost later. Nowadays the term “kerogen” is used to characterize solid organic matter in all sedimentary rocks (Vahur and Eric 2013). Kerogen in oil shale is a complex heterogeneous mixture of organic compounds (Doğan and Uysal 1996). The average molecular weight is in the order of 3000, and an approximate empirical formula would be  $C_{200}H_{300}SN_5O_{11}$  (Khraisha 1998). Siskin and Katritzky (1995) described that HCs are rich in the structure of oil shale kerogen and proposed a kerogen model, shown in Figure 2A, as  $C_{647}H_{1017}N_{19}O_{17}S_4$ . Because kerogen has a huge molecular weight of its component compounds, it is insoluble in normal organic solvents. Bitumen and/or pre-bitumen, which are known as the soluble portion of kerogen, may also exist but in relatively lower amounts (Ronghua et al. 2014, Haifeng et al. 2015). Organic matter in oil shale includes the remains of

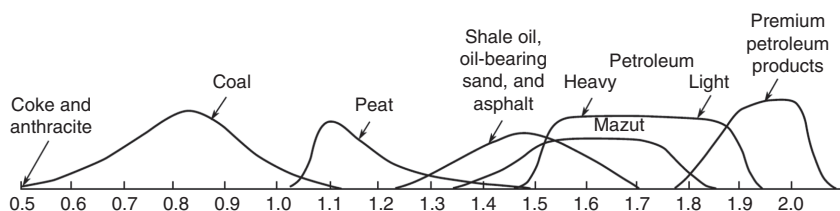
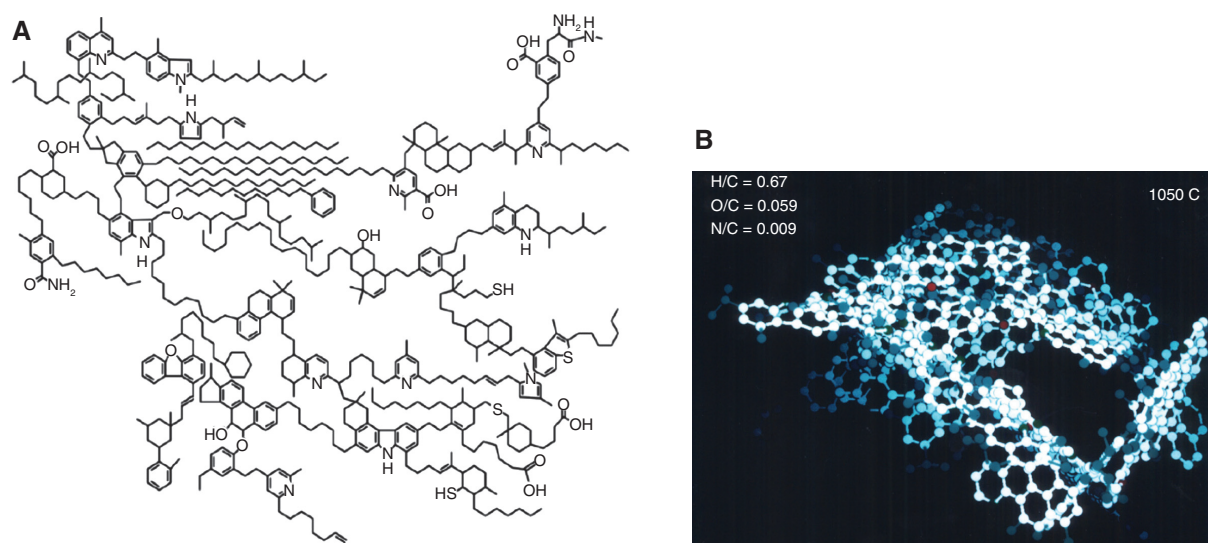


Figure 1: H/C atomic ratios in various hydrocarbon materials (Strizhakova and Usova 2008).



**Figure 2:** (A) Oil shale molecular model  $C_{645}H_{1017}O_{17}S_4N_{15}$  proposed by Siskin and Katritzky (1995) and Xiaoping et al. (2015). (B) 3D representation, using the XMol software, of a type III kerogen structure at the end of catagenesis. Only C atoms (aromatic in white, aliphatic in blue), O atoms (in dark green) and N atoms (in red) are represented. Published lengths and directions for covalent bonds are used, but energy minimization calculations are not performed on the resulting structure. However, it is expected to make little difference due to high aromaticity. (Reproduced with permission from Elsevier; Vandenbroucke 2003, Vandenbroucke and Largeau 2007).

algae, spores, pollen, plant cuticle and corky fragments of herbaceous and woody plants, and other cellular remains of lacustrine, marine and land plants. Small amounts of plant resins and waxes also contribute to the organic matter. Fossil shell and bone fragments composed of phosphatic and carbonate minerals, although of organic origin, are excluded from the definition of organic matter used herein and are considered to be part of the mineral matrix of the oil shale (Dyni 2003). These materials are present as a complex combination of carbon, hydrogen, sulfur and oxygen (Jiang et al. 2007).

The composition and properties of kerogen vary somewhat from deposit to deposit, but may also vary within a deposit. Therefore, the properties of kerogen will be different for the different oil shales. Char is the organic matter that remains in the spent shale after the kerogen is paralyzed. Char also has no fixed composition but depends on the original kerogen and the pyrolysis conditions (Rick et al. 2009). The general term “kerogen” cannot represent a defined chemical structure, unlike other terms such as “protein.” Indeed, the latter corresponds to macromolecules *sensu stricto*, whereas kerogen is a complex combination, via numerous bond types, of a large number of molecular moieties encompassing a wide range of composition and molecular weight (Katti et al. 2014). The chemical structure of kerogen is determined by several main factors; the most important ones are the composition of initial organic matter and its chemical conversion during diagenesis. Different mechanisms (when

acting alone) lead to the formation of absolutely different kerogens with radically different compositions, sets of the main structural fragments and ways of their linking. These kerogens have different HC potentials and the main courses of catagenesis (Bushnev and Burdelnaya 2009). Based on the fraction of hydrogen, carbon and oxygen content of the organic matter, kerogens are classified as type I, type II and type III and are derived from different depositional environments (Katti et al. 2014). Type I kerogen is composed dominantly of liptinite (alginite) and has a high atomic H/C ratio. Type III kerogen is derived from terrestrial plant material and has a low H/C ratio. Type II kerogen has intermediate properties between type I and type III and is mainly derived from organic matter deposited in a marine setting (Brown et al. 2000). A possible structure obtained for a type III kerogen at the end of catagenesis is shown in Figure 2B.

#### 1.4 Significance of modeling the pyrolysis kinetics of oil shale

Kinetic models are helpful to optimize product yield, efficient product separation, eliminate harmful byproducts and to find temperature and pressure at which highest yield of desired product may be achieved. Modeling the pyrolysis kinetics of oil shale is significant for designing and operating an energy-efficient pyrolysis process because pyrolysis is a very complicated thermochemical

conversion process (Xiaoshu et al. 2014). The kerogen in oil shale is such a complicated heterogeneous mixture of organic compounds that the reported pyrolysis kinetics is undoubtedly an average for many different reactions that give the oil product. For this reason, the activation energy and frequency factor for the oil evolution process are only “effective” kinetic values for a very complicated reaction system. They can, however, be used in a mathematical model to represent the process. Effective activation energies are extremely useful in modeling a process from an engineering standpoint. Good kinetic data are essential for accurate mathematical modeling of various oil shale processes (Campbell et al. 1978). Parameters calculated from a parallel model will provide more reasonable information for the oil shale retorting process and for recognizing the chemical structure of oil shale kerogen (Bar et al. 1988, Schenk and Horsfield 1993, Shuyuan and Changtao 2003, Shuyuan and Changtao 2004, Tiwari and Deo 2012b).

## 2 Experimental methods to study pyrolysis kinetics of oil shale

Several investigators have modeled pyrolysis kinetics of oil shale utilizing data obtained from systems such as thermogravimetry (TGA), differential analyzers, differential scanning calorimetry (DSC), Rock-Eval analyzer and various other types of reactors (Tables 1 and 2). However, TA is a typical analytical technique to describe the relationship between physical (or chemical) changes and temperature. The advantages of TA include convenience, fast response and fewer samples needed, and thus wide applications in many fields. With the improvement of thermo analysis techniques, TA has been increasingly used as a means of determining kinetic parameters of fuel pyrolysis and combustion (Qing et al. 2007, Sun et al. 2015a). Khraisha (1998) described different types of techniques working in isothermal and non-isothermal conditions used to study the mechanism of the pyrolytic process involved in the breakdown of organic matter in oil shale. For example, TGA-differential thermal analysis (DTA), Fischer assay and fluidized beds were exercised to define the kinetic parameters, as well as to find the quantity and quality of volatile products. Rajeshwar et al. (1979) concluded that thermal extraction of insoluble kerogen from the oil shale matrix is by far the most direct and simplest method for processing oil shales. The TGA-DTA analysis of oil shale samples has been extensively used as a means of determining the characteristics of devolatilization and kinetic parameters (Sun et al.

2014). The pyrolysis of a Yugoslavian oil shale was represented by three alternative mathematical models, which were constructed using previously reported TGA- as well as DSC-derived kinetic parameters, obtained from the non-isothermal pyrolysis of different samples (Skala et al. 1989).

Reynolds et al. (1995) examined three California shales by programmed temperature micropyrolysis to determine laboratory pyrolysis kinetics, which measures HC evolution using a flame ionization detector. The pyrolysis kinetics were measured by the Pyromat II micropyrolyzer (Lab Instruments, Kenwood, CA, USA) to study oil shales, petroleum source rocks, coals and bitumen, in attempts to understand the process of kerogen maturation and HC generation. The three California samples were analyzed by pyrolysis-mass spectroscopy (MS) utilizing the Pyromat II interfaced with a VG Instruments Micromass residual gas analyzer (Fisons Instruments, Danvers, MA, USA). This technique has been described in detail elsewhere (Burnham et al. 1992b). Stankiewicz and Kruege (1994) analyzed two samples representing type II-S kerogen by pyrolysis-gas chromatography-mass spectroscopy (Py-GC-MS) (CDS 120 pyroprobe, 465, CDS Analytical, Oxford, PA, USA) and revealed that  $C_1$ – $C_5$  alkylpyrroles (as well as  $C_1$ – $C_4$  alkylthiophenes) were major products in the flash Py-GC-MS analysis of a Naples Beach kerogen.

### 2.1 Isothermal and non-isothermal TGA measurements

Mechanisms of kerogen decomposition have been the subject of numerous studies (almost all cited articles), including many different experimental techniques, and have involved both isothermal and non-isothermal procedures (Vahur and Eric 2013). Rajeshwar (1981) analyzed the factors influencing kinetic data such as sample holder geometry, heating rate and atmosphere using non-isothermal measurements instead of isothermal to overcome the significant errors (sample heat-up time, introduction of correction factor in certain cases and the large sample size) in the kinetic data. However, the most effective method for determining the most probable kinetic mechanism of polymer decomposition (kerogen is a complicated polymer with a kind of three-dimensional structure; Shuyuan and Changtao 2003, Tiwari and Deo 2012b) is a combined kinetic analysis of isothermal and non-isothermal TGA measurements. For example, Campbell et al. (1978) and Torrente and Galán (2001) performed such a combined analysis.



Table 1: Critical analysis of kinetic models.

Sr. no.	Sample	Experimental conditions and techniques	Proposed models	Results/remarks	References
1	Colorado oil shale	TGA non-isothermal analysis; 2°C min <sup>-1</sup> . TGA isothermal analysis; 350–424°C. Modified Fischer assay apparatus was used, oil shale sample size of <800 µm, sample weight of 60–80 mg. Inert gas was constantly flowing through the apparatus during these experiments.	Kerogen $\xrightarrow{k}$ Bitumen $\xrightarrow{k'}$ Oil	The results show the reliability and convenience of non-isothermal kinetic experiments in studying oil shale decomposition reactions. Non-isothermal experiments more accurately simulate actual conditions of aboveground and <i>in situ</i> oil shale retorting. These kinetics are “effective” values and can only properly be used to describe the macroscopic oil-production process rather than the complex microchemistry.	(Campbell et al. 1978)
2	Green River oil shale	TGA non-isothermal analysis; temperature range of 25–800°C, ambient inert gas stream (nitrogen), sample weight of 10–20 mg.	Oil shale kerogen $\xrightarrow{k_1}$ pyrolytic bitumen $\xrightarrow{k_2}$ oil+gas+semi-coke residue	The kinetic parameters do not show a systematic dependence on heating rate. This is compelling proof that the derived parameters refer to distinct chemical processes rather than to processes such as product diffusion from the shale matrix. A key feature of this study is also a choice of sample holder geometry and sample mass which facilitates good atmosphere control and easy escape of product gases.	(Rajeshwar 1981)
3	Green River oil shale	The retorts have been operated using shale with grades ranging in Fischer assay from 42 to 152 L/Mg (10–36 gal/ton); gases such as air, air and steam, air and N <sub>2</sub> , air and recycle, O <sub>2</sub> and steam, O <sub>2</sub> and CO <sub>2</sub> , and N <sub>2</sub> alone; gas fluxes ranging from 0.25 to 1.35 mol m <sup>-2</sup> s <sup>-1</sup> (1.2–6.3 scfm/sq ft); shale particles as large as 30 cm (12 in.); and shale bed void fractions from 0.49 to 0.29. An attempt was made to simulate adiabatic conditions in all runs with heating coils located at the top and bottom and along the walls of the retort.	LLNL has developed a one-dimensional mathematical model to simulate modified <i>in situ</i> (MIS) retorting of oil shale.	The model was used to predict the results for MIS retorting on a commercial scale, focusing on larger retorts and larger shale particle sizes than could be investigated experimentally but the model was not strictly accurate in all aspects of retorting.	(Braun et al. 1984b)
4	Green River oil shale	Aboveground retorting using internal combustion in a moving packed-bed retort. Average conditions for the base group of eight Paraho runs are grade (gal/ton) = 27.0, raw shale organic carbon (wt%) = 11.8, raw shale mineral CO <sub>2</sub> (wt%) = 17.7, shale velocity (m/d) = 45.4, bed void fraction = 0.45, cooling at air distributors (kJ m <sup>-2</sup> s <sup>-1</sup> ) = 27.0.	The one-dimensional mathematical model developed at the LLNL to simulate the detailed chemical reaction kinetics involved in MIS retorting of oil shale has been applied to simulate aboveground retorting in a moving, packed-bed retort	Application of the model to a hypothetical set of commercial-scale conditions helped to identify key design parameters. The comparisons (data from the Paraho semiworks retort) illustrated the validity of the model in calculating retort temperature profiles, oil yields, off-gas composition and outlet shale composition. The model calculations pointed out further resolution, namely,	(Braun et al. 1984a)

Table 1 (continued)

Sr. no.	Sample	Experimental conditions and techniques	Proposed models	Results/remarks	References
5	Green River oil shale	The kinetics and product yields calculated by the model are compared to experimental results for pyrolysis conditions ranging from isothermal fluid-bed to high-pressure slow-heating-rate retorting	Governing equations for the model are written as 67 first-order, nonlinear, ordinary equations specifying the rate of change of each gas, liquid and solid component in terms of the vaporization or chemical reactions. This set of equations is solved simultaneously by Livermore Solver for Ordinary Differential Equations on a Cray-1 computer. Most runs took between 1 and 3 min of CPU time	(1) the apparent upward displacement of the combustion zone from the air inlet, (2) the loss of heat through the wall of the retort and (3) the possible refluxing of oil mist between the gas outlet and the combustion zone. A central feature of this model is that it divides the oil into 11 boiling-point fractions in order to treat evaporation more rigorously. This feature also allows cracking of heavy fractions to lighter fractions, enabling a calculation of the effect of pyrolysis conditions on the boiling-point distribution of the product oil. The model is tested under a wide range of pyrolysis conditions for which data are available in the literature. The model does very well generally, although certain limitations are demonstrated. It was valid only for Green River oil shale, but it was expected to be easily modified for other oil shales.	(Burnham and Braun 1984)
6	Yugoslavian oil shale	TGA and DSC isothermal and non-isothermal analysis. Isothermal analysis temperatures 673, 708, 748 and 794 K. Non-isothermal analysis heating rates 2, 5 and 10 K min <sup>-1</sup>	$K^* \longrightarrow f_1 B + f_2 P; f_1 + f_2 = 1$ $K^* \xrightarrow{k_1} f_1 B_1 + f_2 P_1 \xrightarrow{k_2} f_1 B_2 + f_2 P_2 \xrightarrow{k_3} f_1 B_3 + f_2 P_3$ $K \xrightarrow{1} f_1 B_1 + f_2 P_1 \xrightarrow{2} f_1 B_2 + f_2 P_2 \xrightarrow{3} f_1 B_3 + f_2 P_3$ $B \xrightarrow{4} f_1 R_1 + f_2 R_2 \xrightarrow{5} f_1 R_3 + f_2 R_4$ <p> <math>K^*</math> and <math>K</math>: Kerogen and bitumen originally present in oil shale  <math>P</math>: All volatilized products formed  <math>B</math>: All non-volatilized products  <math>f_1</math> and <math>f_2</math>: Stoichiometric coefficients </p>	Considered retorting process design as the main goal. The advantages of the MSM (recognized as a suitable standard procedure for modeling the kinetics of pyrolysis of different oil shale types) in predicting the actual heat consumption rates, and in predicting the pyrolysis effects in both non-isothermal and isothermal regimes, appear to be of significance. The results of the modeling and simulation show that the process can be simulated using either simple or complex models.	(Skala et al. 1989)

Table 1 (continued)

Sr. no.	Sample	Experimental conditions and techniques	Proposed models	Results/remarks	References
7	Three Turkish oil shales (Beypazari, Seyitomer and Himmetoglu)	TGA non-isothermal analysis; oil shale samples with three particle sizes of 0.7, 1.3 and 2.6 mm, sample weight of 500 mg, flow rate of helium was kept constant at 12 L h <sup>-1</sup> and temperature range ~27–700°C	$\text{Kerogen} \xrightarrow{k_1} \text{Bitumen} + \text{oil} + \text{gas} + \text{residue}$ $\text{Bitumen} \xrightarrow{k_2} \text{oil} + \text{gas} + \text{residue}$	A first-order overall kinetic expression was found to be adequate for pyrolysis of the three shales studied. The extent of pyrolysis was practically independent of the particle size. Examination of porosities and surface areas of raw and spent shales obtained after non-isothermal pyrolysis up to final temperatures of 400, 550 and 700°C confirmed the TGA finding that the higher the final temperature, the higher the conversion.	(Doğan and Uysal 1996)
8	Jordan shales (EL-Lajjun and Sultani shales)	TGA isothermal analysis; temperature was varied from 375 to 475°C, atmospheric pressure, oil shale sample size of $1.8 \times 10^{-4}$ to $3.55 \times 10^{-4}$ m, sample weight of 0.5 g, nitrogen flow rate is $1.67 \times 10^{-5}$ m <sup>3</sup> s <sup>-1</sup>	$\text{Kerogen} \longrightarrow \text{Bitumen} + \text{gas}$ $\text{Bitumen} \longrightarrow \text{Oil} + \text{gas} + \text{char}$	Kinetic parameters, weight vs. time data were obtained at temperatures from 375 to 475°C. The rate of kerogen decomposition can adequately be described by a simple mechanism involving first-order kinetics. Possibly, two consecutive first-order reactions may take place during the decomposition process.	(Khraisha 1998)
9	Eight Turkish oil shale	TGA and DTG non-isothermal analysis; sample weight of 10 mg, samples particle size <60 mesh, heating rate of 5°C min <sup>-1</sup> , temperature range of 20–600°C and 50 mL min <sup>-1</sup> gas flow rate (air and nitrogen)	$\text{Kerogen} \xrightarrow{k_1} \text{Bitumen} \xrightarrow{k_2} \text{Oil, gas}$	Kinetic parameters (both pyrolysis and combustion) of oil shale samples were determined using five different methods. Differences between the activation energy values of the samples were observed. At the same time different degrees of maturity and structure of oil shales affected the results.	(Kök and Pamir 2000)
10	Spanish oil shale (Puertollano in Ciudad Real)	TGA isothermal analysis; different particle sizes ( $0.250 \times 10^{-3}$ , $0.505 \times 10^{-3}$ and $0.925 \times 10^{-3}$ m), three temperature plateaux (703, 688 and 673 K). TGA non-isothermal analysis; different heating rates (5, 10, 15, 20 and 50 K min <sup>-1</sup> ) up to 1173 K and for a particle size of $0.250 \times 10^{-3}$ m	$\text{Oil shale kerogen} \xrightarrow{k_1} \text{pyrolytic bitumen}$ $\xrightarrow{k_2} \text{oil} + \text{gas} + \text{semi-coke residue}$	The kinetics are “effective” values (useful for modeling a complex chemical process) which may only be used to describe the macroscopic kerogen decomposition process rather than the microscopic chemistry involved. The integral method yields lower deviation and hence provides a better fit of the data.	(Torrente and Galán 2001)
11	Huadian oil shale	Pyrolysis characteristics studied by TGA, different particle size diameters, under nitrogen atmosphere, heating rate of 40°C min <sup>-1</sup>	$\text{Kerogen} \xrightarrow{k_1} \text{Bitumen} \xrightarrow{k_2} \text{Oil, gas}$	A comprehensive utilization technology for Huadian oil shale resources is recommended for shale oil production, electricity generation, oil shale ash processing, economical efficiency and environmental protection.	(Jiang et al. 2007)

Table 1 (continued)

Sr. no.	Sample	Experimental conditions and techniques	Proposed models	Results/remarks	References
12	Kukersite oil shale	Isothermal retorting; 500 mL aluminum retort, the initial material applied was dry powdered kukersite with kerogen content 32.3%. The isothermal period was kept for 20 min. The nominal temperatures applied were chosen in the region optimal for formation of TB (thermobitumen) 370–410°C	<p>Kerogen <math>\xrightarrow{k_1}</math> TB <math>\xrightarrow{k_4}</math> Volatile</p> <p>Kerogen <math>\xrightarrow{k_2}</math> Volatile</p> <p>TB <math>\xrightarrow{k_3}</math> Coke</p>	A first-order parallel-consequent kinetic model was deduced for preliminary description of the co-effect of time, nominal temperature and heating rate on the yield of products at low-temperature pyrolysis of kukersite in laboratory retorts. The maximum total yield of TB (thermobitumen) and oil from kerogen (91%) was obtained at nominal temperature 410°C after 40-min processing. The calculated kinetic parameter results were compared with the experimental curve of TGA analysis and also among themselves. A root mean square error was calculated for each method and the integral method model was found to be the closest to experimental data, while no relationship was observed between activation energy and the heating rate.	(Johannes and Zaidentsal 2008)
13	Jordan shales (EL-Lajjun)	TGA non-isothermal analysis; oil shale samples size of 50 $\mu\text{m}$ , sample weight of 8–15 g, nitrogen gas is used at 100 mL $\text{min}^{-1}$ , heating rates of 5, 10, 15 and 20°C $\text{min}^{-1}$	<p>Kerogen <math>\longrightarrow</math> Bitumen + gas</p> <p>Bitumen <math>\longrightarrow</math> Oil + gas + char</p>	The calculated kinetic parameter results were compared with the experimental curve of TGA analysis and also among themselves. A root mean square error was calculated for each method and the integral method model was found to be the closest to experimental data, while no relationship was observed between activation energy and the heating rate.	(Shabbar et al. 2011)
14	Mahogany zone of the Green River formation	TGA non-isothermal analysis; oil shale sample size of $1.49 \times 10^{-4}$ m, weight of samples 20–30 mg, elemental analyses of the samples were performed using LECO CHNS-932 and VTF-900 units, nitrogen environment, seven different heating rates range from 0.5 to 50°C $\text{min}^{-1}$ .	Kerogen $\longrightarrow$ Decomposition products	The RMS errors between the experimental and model values for the isoconversion approach produced the lowest RMS values in both rates and cumulative conversion. Isoconversion models are in theory “kinetic model” free and their applicability to the decomposition of a complex material such as kerogen is excellent. However, their applicability in reproducing multistep kinetics has been questioned. Application of these models to real-life processes requires extending these models outside of the experimental data range from which they were derived.	(Tiwari and Deo 2012b)
15	Chinese oil shales (Huadian)	TGA/DTA non-isothermal analysis; ambient atmosphere and nitrogen atmosphere (fluxed by nitrogen with a flow rate of 50 $\text{cm}^3 \text{min}^{-1}$ , oil shale sample size of 63 $\mu\text{m}$ , sample weight of 4 mg, heating rate was kept as 10°C $\text{min}^{-1}$ , temperature range from ambient to 800°C.	<p>Kerogen <math>\longrightarrow</math> Bitumen + gas</p> <p>Bitumen <math>\longrightarrow</math> Oil + gas + char</p>	The analytical model is successfully validated by both experimental data and the numerical model ( $R^2 > 0.99$ ). Some generalizations and extensions of representative kinetic models in wide-area applications are presented. There is a need for such models in fuel and energy technology.	(Xiaoshu et al. 2014)



**Table 2:** Summary of graphical methods to determine kinetic parameters.

Sr. no.	Experimental technique/method	Modeling techniques/methods	Relative error/remarks	References
1	TGA Non-isothermal	Arrhenius, Coats Redfern and Freeman Carroll techniques have been applied Differential method developed by Freeman Carroll	The kinetic parameters do not show a systematic dependence on heating rate. This is compelling proof that the derived parameters refer to distinct chemical processes rather than to processes such as product diffusion from the shale matrix. A key feature of this study is also a choice of sample holder geometry and sample mass which facilitates good atmosphere control and easy escape of product gases.	(Rajeshwar 1981)
2	TGA and DSC Isothermal and non-isothermal	Non-isothermal TGA analysis: using the Doyle-Gorbachev and integral method	Applying the statistical procedure, the slope and intercept of the linear part of the plot determine the activation energy (E) and frequency factor (A).	(Skala et al. 1988)
3	TGA Non-isothermal	Coats Redfern method	The integral method gives the graphical representation to achieve required kinetic data.	(Ahmad and Williams 1998)
4	TGA Isothermal and non-isothermal	Arrhenius and Coats Redfern	The decomposition of oil shale kerogen in terms of a first-order reaction appears to be a suitable assumption since a value of $n = 1$ offers a best fit regression line giving a correlation coefficient of 0.999.	(Williams and Ahmad 2000)
5	TGA Non-isothermal	Arrhenius and integral method	The assumption of a first-order reaction appears reasonable, because the regression correlation factor exceeded 0.95.	(Iaber and Probert 1999)
6	TGA Non-isothermal	Flynn's isoconversional method, Coats Redfern or Piloyan-Novikova methods	The maximal relative error of the weight loss for the organic decomposition stage, calculated by means of the set of kinetic parameters, is 4.9% at 429.85°C.	(Gersten et al. 2000)
7	TGA Non-isothermal	Arrhenius and integral method	The assumption of a first-order reaction appears reasonable: the regression correlation factor exceeded 0.95.	(Iaber and Probert 2000)
8	Fixed bed retort	A modified first-order kinetic equation with variable activation energy is employed to model the total weight loss of El-Lajjun oil shale samples	The obtained kinetic data are modeled using variable heating rate, pyrolysis temperature and variable activation energy principle in a nitrogen sweeping medium. Good fit to the obtained experimental data is achieved.	(Omar et al. 2010)
9	TGA Non-isothermal	Integral method	Closely simulates the conditions that would be found in commercial scale retorts. The regression correlation factor was > 0.95.	(Iaber et al. 1999)
10	Isothermal retorting	Arrhenius method	A step-by-step mathematical model was deduced for description of the co-effect of time, temperature and heating rate at low temperature (370–410°C)	(Johannes and Zaidentsal 2008)

## 2.2 Advantages of non-isothermal conditions

In non-isothermal TGA, the solid is submitted to a gradual increase in temperature (usually linear with time), and in this case it is possible, in principle, to obtain the kinetic parameters (activation energy and pre-exponential constant) with a single experiment. Non-isothermal TGA allows for a wide range of temperatures to be covered, which is not always possible in isothermal TGA, particularly at high temperatures, since significant solid conversion may occur during temperature stabilization at the beginning of the experiments (Brown et al. 2000). On the other hand, one of the problems associated with rising temperature experiments is that the kinetic parameters obtained are frequently dependent on some procedural factors (heating rate, initial amount of solid sample, gas phase composition, reactor geometry, particle size, solid porosity). However, this situation also arises in isothermal studies (Órfão and Martins 2002).

The non-isothermal method has the advantage of shorter experimental time and eliminates the difficulties associated with the isothermal method due to the initial heat-up period. Since a sample may undergo significant reaction while being raised to the temperature of interest, the results obtained by the isothermal method are often questionable (Rajeshwar 1981). The non-isothermal technique has been preferred by some researchers because of its advantages over the isothermal method. Some of the major advantages of non-isothermal technique are the elimination of errors due to the thermal induction period, maintaining a constant heating rate is less demanding compared to retaining a constant temperature environment during an experiment (especially when exothermic reactions are involved), permits a rapid scan of the whole temperature range of interest and it also simulates conditions expected in large scale oil shale retorting processes more closely (Ahmad and Williams 1998, Torrente and Galan 2001, Shabbar et al. 2011, Tiwari and Deo 2012b).

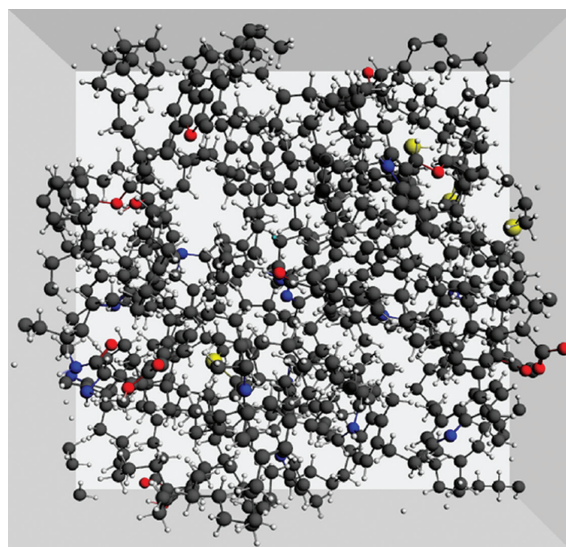
## 3 Oil shale pyrolysis mechanism and kinetics

### 3.1 Oil shale pyrolysis mechanism

The thermal decomposition of coal, kerogen and most synthetic polymers involves a complicated set of concurrent and consecutive initiation, propagation and termination

reactions (Burnham and Braun 1999). Oil shale retorting theories (Hubbard and Robinson 1950, Khraisha 1998, Xiaoshu et al. 2014) explain the conversion of kerogen into shale oil as a two-stage process. Generally, thermal decomposition of oil shale yields volatile materials in the form of oil and gas and a solid residue of char (Shabbar et al. 2011). The pyrolysates of oil shale result mainly from the rupture of weak chemical bond, probably the rupture of weak cross-linked bonds, such as C–O and C–S bonds, and/or the rupture of branched functional groups in the kerogen long molecular structure. These weak bonds have low rupture energy which commensurate with pyrolysis gaseous products such as  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2$  and light HCs. The medium activation energy values are associated with breakdown of the side chains in  $\beta$ -site of aromatics, decomposition of normal alkane with large molecular weight, Diels-Alder cyclization reaction and the rupture of alicyclic HC (Deepak and Eric 1987, Omar et al. 2010).

Xiaoping et al. (2015) carried out molecular dynamics (MD) simulations using a reactive force field (ReaxFF) method for Green River oil shale as shown in Figure 3. The model demonstrates that the thermal decomposition of the oil shale molecule is initiated with the cleavage of the oxygen bridge (C–O bond) and the first product is formaldehyde ( $\text{CH}_2\text{O}$ ). The simulation results show that the C–O bond is weaker than the other bonds, agreeing with its smaller bond dissociation energy. The ring-opening position of the aliphatic ring is usually determined by the stability of free radicals formed in this process. For aromatic HCs, the long-chain substituents are found to be easier to leave and the cleavage of C–C bonds leads



**Figure 3:** Model applied to ReaxFF MD simulations of thermal decomposition (Xiaoping et al. 2015).

to a series of chain reactions and the formation of small fragments, such as ethylene and propylene. The bond cleavages are almost in accordance with the minimum bonding energy rule. NVT (constant volume and constant temperature) simulations show that the pyrolysis process progresses in two stages: the decomposition of kerogen into heavy ( $C_{40+}$ ) species and then the generation of light compounds. Recombination and rearrangements of different fragments are also observed via MD simulations. The main HC fragments of  $C_{10}$ – $C_{20}$  are regarded as the component or precursor of diesel oil. The formation pathways of typical aromatic components are analyzed by tracking the motion trajectories of relevant structures. The products obtained from the simulations were similar to the result of GC-MS analysis, including a great amount of alkanes, olefins and aromatic compounds (Xiaoping et al. 2015). In addition, the main components of the diesel oil were observed in the simulation process, indicating that the ReaxFF simulations can reproduce the experimental results under a suitable NVT simulation temperature and time. Tissot and Welte (1984) classify kerogens as types I, II and III based on their pyrolytic HC yield per total organic carbon (TOC). Although Fischer assay pyrolysis has been the standard for measuring oil yield from oil shale, Rock-Eval analysis is more commonly used in petroleum geochemistry, and the two methods correlate well after making adjustments for gas yields. Type I kerogens yield 650–1000 mg HC/g TOC, and type II kerogens yield 300–650 mg HC/g TOC. Several investigators tried to describe the pyrolysis mechanism of type I kerogen (McKee and Lyder 1921, Johnson et al. 1975, Ziegel and Gorman 1980, Burnham et al. 1996, Freund et al. 2007, Burnham 2010, 2015, Le et al. 2013), and many others analyzed type II kerogen as well (Coburn et al. 1988, Burnham 1990, Castelli et al. 1990, Braun et al. 1991, Burnham et al. 1992a, Freund et al. 1993, Behar et al. 2008). McKee and Lyder (1921) explained the breakdown of oil shale as halving two steps, Eq. (1): the initial formation of heavy bitumen and the next conversion of bitumen to oil. The description of their experiments was formally correct; some had extended the observation to a sequential chemical reaction mechanism:



Although it is pervasive in the oil shale and petroleum geochemistry literature, it is simple to show that this extension is not rigorously correct.

Ziegel and Gorman (1980) showed that not only were the Braun-Rothman bitumen generation kinetics inconsistent with the bitumen concentrations, but also no good

fit was possible with a strictly sequential model. Instead, they found that the data required an alternate pathway mechanism of the form



It merely states that the reactions forming soluble products operate in parallel with those generating smaller volatile products. This can be easily understood in the context of mechanistic models of kerogen decomposition and oil generation (Freund et al. 2007), which use real chemical species and not hypothetical species that are really broad mixtures separated by a physical separation (single-plate distillation) that depends on temperature and pressure.

Although numerous workers continue to consider the conversion of kerogen to gas as a sequential reaction involving bitumen intermediate, simple experiments and kinetic modeling shows that such a simple picture is not correct. To be sure, the initial breakdown products are mostly higher molecular weight, and they continue to break down with continued thermal exposure. However, the species normally defined as bitumen and oil have overlapping compositions, and the physical split between the two depends on temperature and pressure. They are not appropriate lumped species for a chemical kinetic model. Furthermore, for most coals and kerogens, the reactions generating fragments small enough to vaporize from pendant groups proceed in parallel. Well-preserved algal kerogens are an exception, and by analogy with linear synthetic polymers, it appears that multiple bonds must be broken to form species small enough to vaporize. This reaction sequence leads to sigmoidal reaction character. Table 1 presents the analyses of several investigators regarding thermal breakdown of oil shale via different experimental procedures and operating conditions.

### 3.2 Oil shale pyrolysis kinetics

As with the mechanistic aspects discussed in the previous section, the results reported by various investigators on the kinetics of decomposition of oil shale kerogen reveal a spectrum of widely differing behavior. This trend is reflected in the postulated decomposition schemes (Table 1), which range from simple one-step consecutive reactions to complicated branched schemes. The papers cited in Table 1 direct that the decomposition process may be viewed as consisting of multiple parallel

reactions with individual activation energies. Shuyuan and Changtao (2003) studied the kinetics of pyrolysis of oil shale samples from Fushun, Maoming and Huangxian (People's Republic of China) using TGA. They concluded that the dependence of the degree of kerogen conversion into shale oil and gaseous products on activation energies has an exponential character. They found that the reactions of pyrolysis with low activation energies result from the rupture of the weakest chemical bonds. The reactions of pyrolysis with medium activation energies involve the rupture of side chains in aromatic compounds (at the  $\beta$  position), the cleavage of high-molecular-weight alkanes, cyclization reactions and the cleavage of alicyclic HCs, which are accompanied by the release of shale oil. The aromatization of alicyclic compounds, dehydrogenization, polymerization and the decomposition of heterocyclic compounds belong to the reactions of pyrolysis with high activation energies.

The temperature is an important determinant parameter for activation energy and pre-exponential coefficient, and accurate estimates of their temperature dependence are critical to understanding thermal activation processes (Jian et al. 2010). There is a wide variation in the literature for values of activation energy. The type of oil shale and type of pyrolysis, whether isothermal or non-isothermal, are influential factors for the discrepancies. Since a sample may undergo significant reaction while being raised to the temperature of interest, the results obtained by the isothermal method are often questionable. However, this error may be minimized by very rapid heating to the desired isothermal temperature (Doğan and Uysal 1996). Skala and Sokic (1992) developed a kinetic expression commonly used in the TA of oil shale pyrolysis. This was derived on the basis of a simple first-order kinetic equation of kerogen decomposition. The obtained results show that the largest activation energies were detected by using isothermal TG, while combined non-isothermal and isothermal TG gave the smallest values. In all the examined samples and TG analyses performed, there was an increase in the activation energy with increased content of paraffinic structures in the oil shale.

The kinetic parameters do not show a systematic dependence on heating rate. This is a compelling proof that the derived parameters refer to distinct chemical processes rather than to processes such as product diffusion from the shale matrix (Rajeshwar 1981). Although some attempts (Doğan and Uysal 1996, Jaber and Probert 1999) have been made to understand the complex nature of decomposition of kerogen involving numerous organic compounds, some authors have found it sufficient to consider a global first-order kinetic expression to represent

the overall decomposition rate of kerogen through experiments with small particles. Indeed, an overall kinetic expression may be quite reliable, especially for most engineering purposes. But the thermal decomposition of coal, kerogen and most synthetic polymers involves a complicated set of concurrent and consecutive initiation, propagation and termination reactions. Consequently, essentially none can be described by a first-order reaction. Therefore, using a first-order analysis method such as Coats Redfern (Coats and Redfern 1964) on single-heating-rate data will not result in meaningful kinetic parameters, and the ICTAC Kinetics Committee (Brown et al. 2000, Vyazovkin et al. 2011, 2014) specifically discouraged that approach. Reporting Coats Redfern A and E values at multiple heating rates makes no sense whatsoever (Vyazovkin et al. 2011, 2014).

Mohammad et al. (2011) studied the effect of mineral matter content on the activation energy of oil shale pyrolysis. Mineral content of oil shale plays a vital role in HC evolution and pyrolysis reactions. Both activation energy and pre-exponential factor for oil shale and isolated kerogen pyrolysis are found to increase with the increase of heating rate due to heat and mass transfer effects. The derived values of the apparent activation energy are consistent with a first-order reaction. The mean values of activation energy are found to be 75 and 95 kJ mol<sup>-1</sup> for raw oil shale and isolated kerogen pyrolysis, respectively. It is concluded that the mineral matter in oil shale enhances catalytic cracking as is evident from the reduced E values of oil shale compared with those for kerogen. Skala et al. (1987) reported that the activation energy and frequency factor of kerogen concentrate prepared by acid demineralization are lower than that of raw oil shale. However, Karabakan and Yürüm (1998) found that the activation energy of pyrolysis reactions of raw oil shale from two sources was less than that of carbonate-free oil shale. This indicated that metal cations (M<sup>2+</sup>) in the carbonate minerals might have acted as catalysts in the pyrolysis reactions. On the other hand, they found that the activation energy of pyrolysis reactions of silicate-free oil shale was lower than the activation energy for both raw and carbonate-free oil shale. This was explained by the fact that silicate minerals acted as inhibitors in pyrolysis reactions.

Burnham (2015) analyzed that a significant portion of the diversity of A and E values could be attributed to volatility changes over the wide temperature range of different measurements. Even so, an equal or greater contribution to the variability was attributed to poor methodology, including poor data collection and improper kinetic analysis. Kerogen and coal kinetics are commonly and perhaps usually determined using ramped-temperature



experiments. Kissinger's method (Kissinger 1957) is a very easy and common method of extracting  $A$  and  $E$  values from multiple heating rates. Braun et al. (1991) and Burnham (2000) extended this method to obtain estimates of the Gaussian  $E$  distribution parameter, reaction order and nucleation-growth parameters for distributed and sigmoidal reactivities from the reaction profile widths and asymmetries.

Reactivity diversity can be described by a distribution in  $A$ ,  $E$  or both (Burnham and Braun 1999). A pseudo- $n$ th-order reaction is equivalent to a Gamma distribution in  $A$ . A variety of continuous distributions have been used for  $E$ , with a Gaussian distribution being the most common. However, the reactivity distribution is rarely symmetric, so a Gaussian distribution of pseudo- $n$ th-order reactions is superior. Alternatively, a Weibull distribution is very flexible. However, multiple reaction groups are usually present, which require parallel continuous distribution models. Using a discrete  $E$  distribution is more powerful and is the prevalent choice for petroleum systems modeling. Isoconversional methods are equally powerful and suitable for complex kinetic analysis of fossil fuels (Bai et al. 2015b). Tiwari and Deo (2012b) concluded that the advanced isoconversional method yielded activation energies as a function of conversion in the range of 93–245 kJ mol<sup>-1</sup>. The decomposition process can be viewed as consisting of multiple parallel reactions with individual activation energies. Maximum uncertainties in activation energies computed using the advanced isoconversion method were about 10% of the energy values calculated. There is a wide variation in the literature for the values of activation energy. The type of oil shale and type of pyrolysis, whether isothermal or non-isothermal, are influential factors for the discrepancies.

Because the pyrolysis of type I kerogen is usually dominated by a single apparent activation energy, its pyrolytic character is more consistent as a function of the extent of conversion. The Rock-Eval temperature of maximum reaction rate ( $T_{\max}$ ) is roughly constant at 440–445°C as a function of geological maturity until all oil potential is exhausted. Unfortunately, the Rock-Eval  $T_{\max}$  scale was established prior to accurate temperature measurements, and those values are lower than the true  $T_{\max}$  by 35–38°C. Nevertheless, if one simply makes that correction and assumes  $A = 10^{14}$  s<sup>-1</sup>, one obtains a mean activation energy of about 226.08 kJ mol<sup>-1</sup>. This is within the range of plausible values. Type II kerogens typically have distributed reactivity roughly consistent with a Gaussian distribution of 2% in the activation energy. The Rock-Eval  $T_{\max}$  of immature type II kerogens is typically approximately 420–425°C. Again assuming  $A = 10^{14}$

s<sup>-1</sup>, one obtains a mean activation energy of a little less than 221.90 kJ mol<sup>-1</sup>. In fact, it is equally plausible that the initial mean activation energy for both type I and II kerogens is 221.90 kJ mol<sup>-1</sup> and that the difference in the reactivity is due to  $A = 5 \times 10^{13}$  s<sup>-1</sup> for type I kerogen and  $A = 1.3 \times 10^{14}$  s<sup>-1</sup> for type II kerogen, but whether the reactivity difference is absorbed into  $A$  or  $E$  makes no practical difference for modeling oil shale retorting. Because of the reactivity distribution for type II kerogens, the Rock-Eval  $T_{\max}$  increases to 440–445°C by the end of oil generation. After the completion of oil generation, the Rock-Eval  $T_{\max}$  for both type I and II kerogens continue to increase, reflecting the increasingly difficult demethylation reactions as semi-coke moves toward graphite.

Among the most important factors are the type of sweeping gas, heating rate employed and the final pyrolysis temperature; the oil yield and the extent of any oil cracking are greatly influenced by the peak pyrolysis temperature. The main objective of the sweeping gas is the removal of generated products (Omar et al. 2010). Omar (2006) described that the reaction environment during pyrolysis of oil shale has a significant effect on the liquid product distribution and its sulfur content. The total sample weight loss and the oil yield are affected by the sweeping medium. The type of sweep gas or sweeping mixture employed during pyrolysis influenced the percentages of fractions and the sulfur content. Ekinici et al. (1996) investigated the influences of steam and nitrogen sweep gases in a fixed bed reactor on the oil yield and product distribution. They reported an increase in oil yield and higher concentration of *n*-alkane and an increase in the aromatic character of the non-paraffinic product materials. Hershkowitz et al. (1983) reported a 20% increase in kerogen conversion when hydrogen is used as pyrolysis atmosphere in their study of Colorado oil shale; in addition, they reported 90% organic carbon conversion in the 549.85–599.85°C temperature range. Eastman and Schlenger (1964) obtained 126% (vol.%) oil yield of Fischer assay when they used high hydrogen pressure during pyrolysis. El-hafri et al. (2000) studied the effect of steam on product distribution of oil shale pyrolysis. They found that oil yield increases with the addition of steam to nitrogen sweeping gas.

## 4 Graphical methods to determine oil shale pyrolysis kinetics

An understanding of kinetic parameters, such as activation energy and the frequency factor, may be obtained



by various approaches (Wanjuan et al. 2003). Graphical methods are often used to evaluate goodness-of-fit (Xiaoshu et al. 2014). Table 2 summarizes the work of investigators who used graphical methods to analyze kinetics of oil shale. Rajeshwar (1981) analyzed the weight loss data by direct Arrhenius, Coats Redfern and Freeman Carroll techniques. The direct Arrhenius method and the Coats Redfern method are found to be convenient for the analysis of the data. The Freeman Carroll method is rather more tedious and moreover is of little use in analyzing the early stages of the decomposition. The analysis of the kinetic data by the Freeman Carroll method is shown to confirm the validity of assuming first-order kinetics for the thermal decomposition of Green River oil shale. Doğan and Uysal (1996) used the integral method, and non-isothermal TGA data, to determine the overall kinetics of pyrolysis of three Turkish oil shales. Essentially, either differential or integral methods are applied to analyze non-isothermal experimental data. The integral method is generally accepted as more accurate, but even the approximations used in integration techniques are effective in the final results for kinetic parameters. Khraisha (1998) described the kinetic parameters obtained by weight vs. time data at temperatures 374.85–474.85°C using the Arrhenius method for two different Jordan shales. The rate of kerogen decomposition can adequately be described by a simple mechanism involving first-order kinetics. Possibly, two consecutive first-order reactions may take place during the decomposition process.

Shuyuan and Changtao (2004) carried out pyrolysis experiments on oil shale samples from Fushun and Maoming using a TGA analyzer. The kinetic parameters of oil shale pyrolysis were determined from TGA data by using the integral method, differential method, Friedman procedure, maximum rate method and parallel first-order reaction model. A special regression function was used to calculate the pyrolysis reaction rate. Relative regression coefficients by the integral method and differential method were larger than 0.99. Shabbar et al. (2011) investigated the integral method, direct Arrhenius plot method and method of approximate temperature integral. The calculated kinetic parameter results were compared with the experimental curve of TGA analysis and also among themselves. A root mean square (RMS) error was calculated for each method and the integral method model was found to be the closest to experimental data. Torrente and Galán (2001) studied the kinetics of the thermal decomposition of Spanish oil shale using isothermal and non-isothermal TGA. Three methods were applied for the determination of the kinetic parameters, the direct Arrhenius plot method, the integral method and the differential method. Among

the three models used in non-isothermal conditions, the integral method yields lower deviation and hence provides a better fit of the data.

## 5 Challenges in determination of oil shale pyrolysis kinetics

In the depletion of oil and natural gas resources, challenges related to the conversion of solid fossil fuels (coal, shale and peat) into motor fuels and chemicals have become of considerable practical importance. In particular, interest has quickened in the processing of oil shale, whose geological reserves are in abundance. Some of the experimental and modeling challenges of oil shale pyrolysis kinetics are described below.

### 5.1 Experimental challenges

Isothermal conditions are often difficult to ensure during the entire course of reactions that occur at high temperature. This difficulty is the result of the initial heat-up period required to reach the isothermal reaction temperature (Campbell et al. 1978). A part of the sample may change while the sample is heated to the desired temperature, especially at the degradation of high polymers; this initial structure change in the sample complicates the isothermal data and makes it difficult to analyze (Ozawa 1965). The time required for the test samples to attain the reaction temperature introduces a significant error in the kinetic data, especially at elevated temperatures when the heat-up time becomes a significant fraction of the total reaction period (Rajeshwar 1981, Doğan and Uysal 1996, Jaber et al. 1999).

Thermal methods providing information about net results of mass loss and calculation of kinetic parameters are based on simplifying assumptions, which do not correspond to the complex chemical reactions in the thermal degradation of the oil shale (Kök and Pamir 2000). The use of TGA to determine kinetic parameters for the pyrolysis of oil is complicated in that the oil shales are a complex mixture of kerogen and a wide range of minerals. In addition, the decomposition of the oil shales represents a large number of reactions in parallel and series whilst the TGA measures the overall weight loss due to these reactions. Therefore, the TGA provides general information on the overall reaction kinetics rather than individual reactions, and therefore the activation energies derived from TGA should be termed apparent activation energies

(Ahmad and Williams 1998). Accurate isothermal and non-isothermal operations at large scale are not possible.

## 5.2 Challenges in determination of oil shale pyrolysis mechanism and kinetics

Oil shale pyrolysis is a very complicated thermochemical conversion process involving extremely complex reactions and the end products depend on numerous factors (Tiwari and Deo 2012b, Xiaoshu et al. 2014). Since kerogen is a complex heterogeneous mixture of organic compounds with an approximate formula of  $C_{200}H_{300}SN_5O_{11}$  (Khraisha 1998), its decomposition includes a very complex reaction, or group of reactions, that results in the production of different types of products ranging from a single carbon atom per molecule ( $CH_4$ ) to compounds containing more than 30 atoms per molecule (Khraisha 1998). The wide variety of products obtained by the thermal processing of oil shale pose difficulties in the determination of the kinetics and mechanism of pyrolysis (Kök and Pamir 2000).

Apart from the decomposition of the oil shale kerogen, there are a variety of other reactions that are brought about by application of heat. For example, the presence of host minerals in the relevance of measured parameters to on-field applications of oil shale matrix significantly complicates the thermal behavior. These reactions are critically dependent on the nature of the atmosphere surrounding the shale. The complexity of the kerogen decomposition process is compounded by the presence of secondary reactions which include secondary cracking and polymerization. The rate of heating and the possible catalytic effects of mineral matter are additional complicating factors (Rajeshwar et al. 1979). The complex reaction schemes of oil shale pyrolysis have been presented in Table 1.

Different mechanisms, with various degrees of complexity, have been proposed to describe oil shale pyrolytic behavior. Generally, these are based on tracking intermediate, primary and secondary pyrolysis products, often without a clear identification of all of the products in any of the classes being tracked. Kinetic parameters have been calculated by fitting experimental data to an assumed semi-empirical model of the pyrolysis process. There is, thus, not surprisingly a large variation in reported kinetic parameters (activation energies and frequency factors). Consequently, the results are often of limited generality, applicable to the particular experimental conditions studied, often potentially influenced by heat and mass transfer limitations on observed kinetics (Vahur and Eric 2013).

The structure and composition of the organic matter (kerogen) are not yet well established. The product distribution shows a uniform trend that is not quantitative. Secondary reactions occur during the process through complicated mechanisms.

## 5.3 Challenges of graphical methods

Graphical methods are although simple, an obvious disadvantage with these methods is to describe observations of the data only without showing the underlying mechanism by which the data are produced. Another relevant disadvantage, which is directly tied to these methods, is that graphical methods generally suffer from poor statistical properties (Burnham and Braun 1999, Xiaoshu et al. 2014).

## 5.4 Modeling challenges

The structure and composition of the organic matter (kerogen) are not yet well established. Thus the modeling of oil shale pyrolysis kinetics is extremely complicated (Bai et al. 2014). Vandenbroucke (2003) described that the name kerogen, in opposition with usual chemistry nomenclature, does not represent a substance with a given chemical composition. Indeed kerogen is a generic name, in the same sense as lipids or proteins. Vandenbroucke and Largeau (2007) explained that the general term “kerogen” cannot represent a defined chemical structure. In fact, “true” macromolecular components of kerogen cannot be represented because their molecular composition is not known. Only chemical structures like those of synthetic polymers, where a small sub-unit repeats the whole structure, can be represented by a detailed chemical structure. Chemical structural information about kerogen is critical for assessing the thermal maturity of source rocks and evaluating the HC generation potential. However, knowledge of the detailed chemical changes of kerogen with increasing thermal maturity remains insufficient (Vandenbroucke 2003, Vandenbroucke and Largeau 2007).

A single approach to the thermal processing of oil shale is difficult to determine, and process parameters and implementation are difficult to optimize because of differences in the composition and properties of oil shale from various deposits. The composition and quantitative ratios between the pyrolysis products of oil shale depend on many factors: the type and origin of the organic matter of oil shale, the final process temperature, the rate of

heating, the residence time in a high temperature zone, grain size, composition and pressure (Strizhakova and Usova 2008).

Many mechanisms could be postulated. Parameters in mathematical models can force a good fit, but this does not mean that the model is unique. Reliable kinetic data are essential for the accurate mathematical modeling of various on-surface and *in situ* oil shale processes. Due to the very complex nature of the organic matter in oil shale, unraveling the kinetics has not been straightforward. An accurate kinetic model that is able to adequately represent the mechanism of kerogen conversion to generated products is necessary.

Most of the developed kinetic models by the researchers have limited application.

## 6 Discussion and summary

Since an accurate Arrhenius model equation is inherently nonlinear in nature allowing no exact analytical solution, numerical techniques become necessary to find the solutions and the parameters (e.g. Youtsos et al. 2013). To determine an appropriate valid reaction model, one of several available methods, which could be sigmoidal, distributed reactivity or multiple reactions depending on the material are used. Valuable insights are available through isoconversional (Burnham and Braun 1999, Brown et al. 2000, Vyazovkin et al. 2011), extended Kissinger (Burnham and Braun 1999, Burnham 2000) and generalized reaction profile (Gotor et al. 2000) methods. Also, look for inflection points diagnostic of multiple reactions. One cannot determine the correct model from sparse data where the maximum conversion varies substantially with temperature.

Shale oil produced by pyrolysis is the result of several physical and chemical reactions occurring in series and parallel (Jaber and Probert 1999, 2000, Jaber et al. 1999). The simple model is usually inappropriate for the simulation of pyrolysis over a full range of conditions, so more detailed representation of the pyrolysis process is necessary by combining parallel and consecutive reaction steps (Bar et al. 1988, Schenk and Horsfield 1993, Shuyuan and Changtao 2003, 2004, Tiwari and Deo 2012b). Kinetic parameters calculated from the parallel model will provide more reasonable information for the oil shale retorting process and for recognizing the chemical structure of oil shale kerogen (Bar et al. 1988, Skala et al. 1989, Schenk and Horsfield 1993, Shuyuan and Changtao 2003, 2004, Tiwari and Deo 2012b, Bai et al. 2015a). Skala et al.

(1989) investigated three alternative mathematical models based on single-step, two-step and multistep (MSM) reaction schemes. The advantages of the MSM in predicting the actual heat consumption rates, and in predicting the pyrolysis effects in both non-isothermal and isothermal regimes, appear to be of significance. Shuyuan and Changtao (2003) developed a kinetic model which assumes several parallel first-order reactions with changed activation energies and frequency factors to describe the oil shale pyrolysis.

The correct reaction model was rarely close to first order, with most kerogens requiring a reactivity distribution (Schaefer et al. 1990, Braun et al. 1991, Tegelaar and Noble 1994, Peters et al. 2006) as for coals, and some well-preserved algal kerogens requiring a sigmoidal reaction model (Burnham et al. 1996, Peters et al. 2015). The decomposition temperatures of immature to early-mature coals and kerogens vary by only about 50°C, which corresponds to a change of about 10% in the activation energy or a factor of about 16 in the frequency factor. The range of variability in  $A$  and  $E$  is somewhat larger due to real mechanistic compensation effects. The range of frequency factors is most likely in the  $10^{12}$ – $10^{16}$  s<sup>-1</sup> range, with most values within the middle half of that range. The range of variability in the principal activation energy is from about 200 to 242 kJ mol<sup>-1</sup>, with most samples being in the middle half of that range (Burnham et al. 1987, 1988, Sundararaman et al. 1988, Pepper and Corvi 1995). There is little evidence that the activation energy for conversion of kerogen to bitumen, oil and gas is significantly different from the activation energy for conversion to volatile HCs (<C<sub>32</sub> or so). Realistic kinetic parameters for both kerogen conversion and oil creation are constrained by geological observation of their respective stabilities (Pepper and Corvi 1995).

Only a few attempts have been made to develop an advanced model of oil shale pyrolysis, relevant to the design of industrial scale oil shale retorting (Wallman et al. 1981, Burnham and Braun 1984). Modeling the pyrolysis kinetics of oil shale for understanding the decomposition mechanisms and kinetic parameters is significant for designing and operating an energy efficient pyrolysis process (Skala et al. 1989, Tiwari and Deo 2012b, Xiaoshu et al. 2014). The developed kinetic models have been complex in nature, utilizing intermediates formed from kerogen initial decomposition and the secondary reactions to produce gases and shale oil products (Hubbard and Robinson 1950, Khraisha 1998, Xiaoshu et al. 2014). Lewis and Braun (1981) described a mathematical model, developed at the Lawrence Livermore National Laboratory (LLNL), which is based on an improved understanding of

the physical and chemical processes involved in retorting. It has since been modified to calculate the retorting of shale moving through a retort, as required for a continuous process in surface equipment. First, the model was modified to allow the reacting shale particles to move through the retort at a specified linear velocity, as required for a continuous process in surface equipment. Second, intraparticle thermal conduction was incorporated into the model. Then the shale temperature and composition were determined as a function of radial position within a particle, both by the gas-solid heat transfer coefficient and by the shale thermal conductivity. The developed mathematical model was considered as a powerful tool in the development of retorts, especially in understanding the combined effects of heat-transfer processes and the thermodynamics and kinetics of the many chemical reactions. Thus, it was believed that application of this mathematical model may contribute to improve surface processing.

Tiwari and Deo (2012b) showed that the advanced iso-conversion method provides a combined pre-exponential factor and reaction model as a function of conversion. The RMS errors between the experimental and model values for the different approaches were compared. The iso-conversion approach produced the lowest RMS values in both rates and cumulative conversion.

Globally, single-stage decomposition was assumed in deriving kinetic rate expressions (Tiwari and Deo 2012b).

Kerogen  $\longrightarrow$  Decomposition products. (3)

The conversion of solid matter in shale (kerogen) to products from TGA weight loss data is defined as (Tiwari and Deo 2012b)

$$\alpha = \frac{W_0 - W_t}{W_0 - W_\infty}, \quad (4)$$

where  $W_0$  is the initial weight of the sample (mg),  $W_t$  is the weight of the sample at time  $t$  (mg),  $W_\infty$  is the weight of the sample at the end of the experiment (mg) and  $\alpha$  is conversion.

In general, the rate of decomposition can be expressed using the non-parametric kinetic equation

$$\frac{d\alpha}{dt} = f(T) \cdot f(\alpha). \quad (5)$$

Using the Arrhenius expression leads to the following:

$$\frac{d\alpha}{dt} = f(T)f(\alpha) = Ae^{\frac{-E}{RT(t)}}f(\alpha). \quad (6)$$

For a constant heating rate  $\beta = dT/dt$  Eq. (6) may be written as

$$\beta \frac{d\alpha}{dT} = Ae^{\frac{-E}{RT(t)}}f(\alpha). \quad (7)$$

The integral form of this equation after separating variables is

$$\int_0^{\alpha^*} \frac{d\alpha}{Af(\alpha)} = \frac{1}{\beta} \int_0^{T^*} e^{\frac{-E}{RT(t)}} dT = \frac{1}{\beta} [I(E_\alpha, T_\alpha)]. \quad (8)$$

The assumptions that the reaction model does not depend on heating rates and is constant for a small conversion interval lead to the integral form of the rate law:

$$\frac{\alpha_{\text{end}} - \alpha_{\text{start}}}{Af(\alpha)} = \frac{I(E_\alpha, T_\alpha)}{\beta}. \quad (9)$$

These assumptions suggest that the integral at any particular conversion should be the same for all heating programs and be a function of the time-temperature relationship. According to this, for a set of  $N$  experiments carried out at different heating programs, the activation energy is determined at any particular level of conversion by minimizing the following function:

$$\chi^2(E) = \frac{1}{N(N-1)} \sum_{i=1}^N \sum_{j \neq i} \left( 1 - \frac{I_i(E, T)}{I_j(E, T)} \right)^2, \quad (10)$$

where the subscripts  $i$  and  $j$  represent two experiments performed under different heating programs. The trapezoidal rule is used to evaluate the integral numerically and the minimization procedure is repeated for each value of  $\alpha$  to find the dependence of activation energy on the extent of conversion. The activation energy distribution obtained in Eq. (10) may be used to determine  $[A \cdot f(\alpha)]$  as a function of  $\alpha$ .

The experimental rate and conversion data can be reconstructed based on the model parameters using Eq. (7):

$$\ln[\beta i(d\alpha/dT)_{ai}] = \ln[Af(\alpha)] - \left( \frac{E_\alpha}{RT_{\alpha,i}} \right). \quad (11)$$

Kinetic models can be used to extrapolate to non-experimental rates. Slow pyrolysis that is likely during *in situ* oil shale production and high rates of flash pyrolysis are of interest. The assumptions of the isoconversion method [Eq. (9)] allow calculating the temperature to reach a level of conversion at extrapolated heating rates



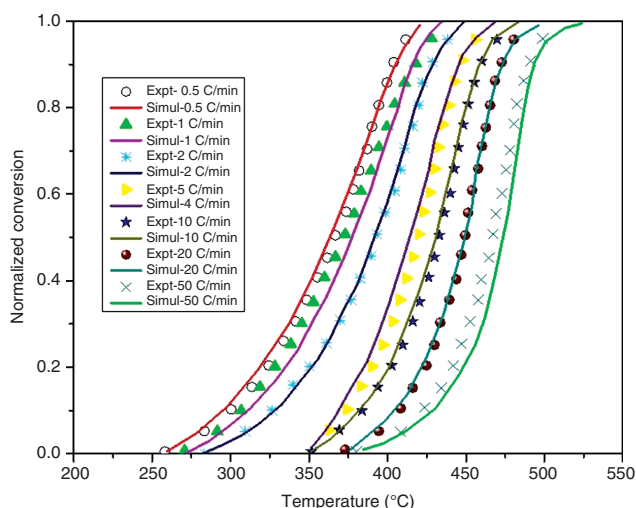
using the following mathematical equivalency (Vyazovkin and Lesnikovich 1992, Tiwari and Deo 2012b):

$$\frac{I(E_a, T_{a,i})}{\beta_i} = \frac{I(E_a, T_{a,j})}{\beta_j}. \quad (12)$$

Eq. (12) was used to estimate the temperature at which the material starts to convert. The procedure for reconstruction was then used to obtain conversions and rates at extrapolated conditions (Tiwari and Deo 2012b).

Tiwari and Deo (2012b) described two distinct data analysis approaches, advanced isoconversional method and parameter fitting, using the TGA dataset of the Green River oil shale. RMS errors between the model and experimental data were the lowest for the isoconversional method, but the distributed reactivity models also produced reasonable results. Simulated decomposition rates and onset temperatures shift to higher temperatures at higher heating rates. When using parameter fitting approaches, a number of models produce similar results making model choice difficult. A MATLAB-based computational method described in the text was used. Results of the model comparisons with the experimental data are shown in Figure 4. The agreement between the model and the experimental data is good over most of the conversion range, and for all the rates. The extrapolated results are not all consistent with some experimental results.

To derive valid kinetic parameters, one must follow the following steps: decouple temperature and conversion, eliminate or measure thermal gradients, determine the reaction model, fit the data, and confirm agreement, which are summarized from guidance in the literature



**Figure 4:** Experimental and simulated conversion profiles at different heating rates using the advanced isoconversional method (Tiwari and Deo 2012b).

(Burnham and Braun 1999, Brown et al. 2000, Burnham 2000, Gotor et al. 2000, Vyazovkin et al. 2011, 2014, Peters et al. 2015).

## 7 Conclusions and recommendations for future work

The study carried out in this research work concludes the following points.

Py-GC-MS is a favorable method to chemically characterize the main structural skeleton in the kerogen at the molecular level. Any improvement in knowledge of kerogen composition and structure may increase the reliability of kinetic models in predicting the amount and composition of generated petroleum products.

Classic graphical methods cannot unambiguously measure and estimate kinetic parameters due to the mathematical complexity. The simple model is usually inappropriate for the simulation of pyrolysis over a full range of conditions. Kinetic parameters calculated from the parallel model will provide more reasonable information for the oil shale retorting process and for recognizing the chemical structure of oil shale kerogen.

Advanced isoconversion methods would be appropriate for the calculation of the distribution of activation energies for multiple reactions involved in the decomposition of complex material such as kerogen to products.

The range of variability in the principal activation energy is from about 200 to 242 kJ mol<sup>-1</sup>, with most samples being in the middle half of that range, while the range of frequency factors is most likely in the 10<sup>12</sup>–10<sup>16</sup> s<sup>-1</sup> range, with most values within the middle half of that range.

Some recommendations that are suggested for further research work to resolve differences in reported kinetics are as follows.

An important shortfall of the presented kinetic models is their limited application. There is a need of such models that are able to fit the data and extrapolate beyond the range of the data, generic and application independent.

Isoconversion models are in theory “kinetic model” free and their applicability to the decomposition of a complex material such as kerogen is excellent. However, their applicability in reproducing multistep kinetics has been questioned. More attempts are required to develop an advanced model of oil shale pyrolysis, relevant to the design of industrial scale oil shale retorting.

The study of mineralogy suggests that additional reactions, dehydration and dehydroxylation, need to be included in the complete pyrolysis mechanism. The



mathematical models need to be improved to account for the thermodynamic behavior of the products formed.

## Nomenclature

$W_0$	Initial weight of the sample (mg)
$W_t$	Weight of the sample at time $t$ (mg)
$W_\infty$	Weight of the sample at the end of the experiment (mg)
$\alpha$	Conversion
$\beta$	Constant heating rate ( $^{\circ}\text{C min}^{-1}$ )
$K^*$	Kerogen and bitumen originally present in oil shale
$P$	All volatilized products formed
$B$	All non-volatilized products
$f_1$ and $f_2$	Stoichiometric coefficients
$t$	Time
$N$	Number of heating rates
$I$	Integral symbol
$T_\alpha$	Temperature at conversion $\alpha$
$R$	Gas constant ( $8.314 \text{ kJ mol}^{-1} \text{ K}^{-1}$ )
$T$	Temperature (K)
$T_{\max}$	Temperature of maximum reaction rate
$E$	Apparent activation energy ( $\text{kJ mol}^{-1}$ )
$E_\alpha$	Activation energy at conversion $\alpha$
$f(\alpha)$	Reaction model
$f(T)$	Temperature dependence of the reaction rate

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## Bionotes



### Muhammad Afzal Raja

Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100049, China; and College of Chemical and Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

Muhammad Afzal Raja is currently completing his doctoral research at the Institute of Process Engineering, University of Chinese Academy of Sciences. His research areas include modeling oil shale pyrolysis and kinetics, process simulation and assessment of hydrogen and high-value hydrocarbon fuel products from oil shale pyrolysis. He served at Pakistan Oilfields Ltd. (May 2011–August 2013) and in Descon Integrated Projects Ltd. (August 2008–April 2013) as a process safety engineer. He received his graduation degree in 2007 from the University of Engineering and Technology, Lahore, Pakistan, and received his Master's degree in 2009 from the University of Punjab, Pakistan. He has two presentations to his credit.



### Yongsheng Zhao

Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100049, China; and College of Chemical and Engineering, University of Chinese Academy of Sciences, Beijing 100049, China

Yongsheng Zhao is currently completing his doctoral research at the Institute of Process Engineering, University of Chinese Academy of Sciences, and he will graduate in June 2017. His major is chemical engineering and technology. His research areas include ionic liquids for various gases absorption and separation: an extensive database with rich data and a systemic screening method. He has published seven SCI papers and one conference paper.



### Xiangping Zhang

Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100049, China  
xpzhang@ipe.ac.cn

Xiangping Zhang received her PhD degree in Chemical Engineering in 2002 from the Dalian University of Technology. Then she joined Institute of Process Engineering of CAS. Her research interests include process integration, thermodynamics and separation engineering. She has published about 130 papers in peer-reviewed journals, and obtained 20 issued Chinese invention patents and 4 issued PCT patents. She was awarded the National Award for Natural Sciences and the Nomination Award of the 4th Top Ten Outstanding Women in Chinese Academy of Sciences in 2012.



### Chunshan Li

Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100049, China

Chunshan Li received his PhD degree in Chemical Engineering from the Institute of Process Engineering in 2006. He was a postdoctoral fellow at Federal Institute for Materials Research and Testing, BAM (2006–2007), and a JSPS fellow at Nagoya University, Japan (2007–2009). He joined IPE, CAS and has been a professor at the Hundred Talents Project of IPE since September 2009. His research mainly focuses on a cleaner energy catalytic process, chemical synthesis, chemical process design and integration. He has published more than 70 peer-reviewed articles in journals such as *AIChE J.*, *Ind. Eng. Chem. Res.* and *Chem. Eng. J.* and holds 29 patents.



### Suojia Zhang

Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100049, China

Suojia Zhang is Professor and Director General of the Institute of Process Engineering (IPE), Chinese Academy of Sciences (CAS), a member of CAS, Director of Beijing Key Laboratory of Ionic Liquids Clean Process, and Director of Professional Committee of Chinese Chemical Society of Ionic Liquids and Green Engineering. He is “National Science Fund for Distinguished Young Scientists” Winner, 973 Chief Scientist, and fellow of the Royal Society of Chemistry. He mainly engages in ionic liquids and green process engineering. He has published more than 300 papers and more than 90 patents, and also edited or written four monographs. He won a number of awards, such as the Second Class Prize of National Natural Science Award in 2010.