

# Hydrocarbon-Generation Kinetics of the Doig Formation, Northeastern British Columbia and West-Central Alberta

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#### Introduction

Reliable petroleum-system models require kinetic parameters of the reaction induced by thermal decomposition of kerogen into hydrocarbons to be calibrated to the source rock (Peters et al., 2018). Formation-specific kinetic parameters for the Doig Formation are not in the public domain; therefore, any previous attempt to model the hydrocarbon generation history would have required kinetic analyses to be undertaken or reliance on analogue data, both of which may produce erroneous results.

The Lower to Middle Triassic Doig Formation of the Western Canada Sedimentary Basin (WCSB) extends continuously across northeastern British Columbia (BC) and westcentral Alberta. Historically, the Doig and the underlying Montney formations were viewed as source rocks for other conventional reservoirs in the basin, mainly in other Triassic and Cretaceous strata (Du Rouchet, 1985; Creaney and Allan, 1990; Riediger et al., 1990; Edwards et al., 1994). With the industry shifting the focus of development to unconventional reservoirs, the Doig Formation has been recognized as an important resource of gas and natural-gas liquids. The Gas Technology Institute (Faraj et al., 2002) estimated the total gas-in-place in the Doig Formation at 4 trillion m<sup>3</sup> (140 tcf), whereas Walsh et al. (2006) estimated the total gas-in-place as ranging from 1.1 to 5.7 trillion m<sup>3</sup> (40–200 tcf). A more recent study by the United States Energy Information Administration (2013) estimated 2.8 trillion m<sup>3</sup> (100 tcf) of gas-in-place for the Doig Phosphate Zone alone.

This paper presents the results of the reaction kinetics parameter modelling for immature rocks of the Doig Formation source rock. The Doig kinetic parameters are compared with those published for other North American shale plays and the variability of activation energies is explained. This study is part of a broader research project on the Doig Formation petroleum system and the results of the reaction kinetics presented here provide the inputs required to proceed with the subsequent steps in modelling thermogenic hydrocarbon generation across the basin.

#### **Geological Framework**

The Doig was deposited in the Middle Triassic, between the Anisian and Ladinian, and is part of the Diaber Group along with the underlying Montney Formation (Figure 1). The sedimentation in the Triassic of the WCSB is marked by a transition from carbonate-dominated intracratonic and passive-margin conditions, predominant during the Paleozoic, to a siliciclastic-dominated, active embryonic foreland basin. The Triassic succession was deposited in a series of three major third- or fourth-order transgressive-regressive cycles (Gibson and Barclay, 1989; Edwards et al., 1994). The interval from the Doig through the Halfway and Charlie Lake formations corresponds to the second cycle and the phosphatic interval at the base of the Doig represents a condensed section formed during the initial transgression of the second cycle (Gibson and Barclay, 1989).

The main elements that influenced the distribution of the Triassic interval were the underlying Devonian Leduc and Swan Hills reefs, and the Mesozoic reactivation of the Mississippian Dawson Creek graben complex (DCGC), which includes the Fort St. John graben and the Hines Creek graben. The DCGC formed in response to localized differential subsidence in the Peace River Embayment. The DCGC faults continued to be active during the Triassic, imposing significant controls on the distribution of sediments (Marshall et al., 1987; Barclay et al., 1990; Davies, 1997; Eaton et al., 1999). The Devonian reefs exerted a topographic influence on Triassic sedimentation by controlling facies changes (Davies, 1997), and may also have influenced subsidence rates and, hence, thickness variation.

The Doig Formation consists of mudstone, siltstone and subordinate sandstone, bioclastic packstone and grainstone, deposited under marine conditions in environments ranging from shoreface through offshore (Evoy and Moslow, 1995). The Doig can be informally subdivided into three units, as proposed by Chalmers and Bustin

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**Figure 1.** Stratigraphic chart of the Triassic, in the subsurface of the Peace River area, northeastern British Columbia and adjacent areas (after Gibson and Barclay, 1989; Golding et al., 2015). Eustatic level based on Hardenbol et al. (1998). Abbreviations: Fm., Formation; Gp., Group.

(2012): the basal unit, Doig A, corresponding to the also informal but widely referred to 'Doig Phosphate Zone' (DPZ), composed of organic-rich radioactive dark mudstone with common phosphate granules and nodules (the DPZ is generally readily distinguishable in well logs by its high gamma-ray signature); the intermediate Doig B, primarily composed of medium to dark grey argillaceous siltstone and mudstone intercalated with localized sandstone; and the upper Doig C, composed of relatively organic-lean siltstone and argillaceous fine-grained sandstone. The DPZ is considered a good to excellent hydrocarbon source rock and an important source for many conventionally hosted hydrocarbons in the basin, including Triassic strata, such as Halfway, Charlie Lake and Doig sands. Previous studies found type II oil and gas-prone kerogen with total organic carbon content ranging from 1.8 to 11 wt. % (Riediger et al., 1990; Faraj et al., 2002; Ibrahimbas and Riediger, 2004).

#### **Material and Methods**

Twenty-three samples were selected for reaction-kinetics analysis through multiple heating-ramp open-system pyrolysis. These samples cover a significant portion of the Doig Formation subcrop area and a wide range of maturities (Figure 2), as well as all its stratigraphic subdivisions (Figure 3). The samples were chosen from among more than 440 analyses carried out on cuttings and whole-rock core using the Rock-Eval pyrolysis method (Espitalié et al.,

1977), based on sharpness and intensity of the kerogen conversion peak, and a wide range of hydrogen index (HI) and oxygen index (OI) values to capture all of the pseudo-van Krevelen kerogen types identified (Figure 4). Samples were classified in discrete kerogen-type categories based on the pseudo-van Krevelen crossplot. Approximately 70 mg of powdered bulk rock (i.e., not concentrated kerogen) of each sample was pyrolyzed, using a HAWK<sup>®</sup> instrument from Wildcat Technologies, at 5°C, 25°C and 45°C per minute to 600-700°C, following an isothermal plateau of up to 260-310°C to purge free hydrocarbons. The pyrolysis curves were trimmed in the time domain and the flame-ionization detector signal was baseline corrected, smoothed, integrated and processed using the commercially sourced Kinetics2015 software (GeoIsoChem Corporation, 2019). Reaction-activation energies and pre-exponential factors were modelled through a distributedreactivity method (Braun and Burnham, 1987; Ungerer and Pelet, 1987) with a fixed activation energy (E) spacing of 1 kcal/mol, and an isoconversional method (Friedman, 1964; Vyazovkin and Lesnikovich, 1988), assuming a series of parallel first-order reactions in 0.01 conversionfraction increments, to determine the variation of activation energy as a function of conversion.

#### **Results and Discussion**

Approximately half of the samples analyzed are of kerogen type II, as determined by hydrogen- and oxygen-index evo-





**Figure 2.** Location of wells from which samples were selected for reaction kinetics analysis in northeastern British Columbia and adjacent area, against a backdrop of the Doig Formation thermal-maturity map (after Silva and Bustin, 2018) and main structural elements that influenced the Triassic deposition (after Davies, 1997). Cross-sections shown in Figure 3 indicated by A–A' and B–B'. Abbreviation: Prec., Precambrian.

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Figure 3. Stratigraphic cross-sections (along strike) of wells in northeastern BC and adjacent area, with the top of the Doig Formation as datum, showing the stratigraphic subdivisions of the Doig and the location of the samples (yellow stars) analyzed for reaction kinetics (location of A–A' and B–B' shown in Figure 2). Abbreviation: GR, gamma ray.







lution paths, whereas one third is of type III. The remaining are classified as type II/III, due to either kerogen mixing, contamination or high maturity causing points to plot too close to the origin. The median value of the activation energy of all Doig samples analyzed ranges from 51 to 67 kcal/mol with a pre-exponential factor that varies from  $5.3 \times 10^{13}$  to  $2.7 \times 10^{18}$  (Figure 5). The correlation between the median activation-energy and frequency factor is log linear, with an  $r^2$  of 0.98. The activation-energy distribution of kerogen type II samples is noticeably narrower than that of type III, with median values ranging from 53 to 63 kcal/ mol. The precision of the global kinetic parameters was determined by repeated analyses of a standard sample. The 95% confidence interval (i.e., two standard deviations divided by the median) is  $\pm 1.2$  kcal/mol around the median activation-energy value of 55 kcal/mol, and within a factor of 2 for the average frequency factor of  $2 \times 10^{15}$ .

There is a clear thermal-maturity influence on the activation-energy distributions, despite a scatter of up to 5 kcal/ mol for a given temperature of maximum rate of hydrocarbon-generation ( $T_{max}$ ) value (Figure 6). The correlation is obscured due to variations in activation energies introduced by mixture of kerogen types during deposition, and possibly to cross-contamination between cuttings samples of different depths containing different kerogen types. Nonetheless, it is possible to distinguish two different trends and generate linear regressions for kerogen types II (blue dashed line in Figure 6) and III (black dashed line in Figure 6), with r<sup>2</sup> values of 0.49 and 0.22, respectively. The lowest maturity samples analyzed in this study, for which kerogen type can be determined with reasonable confidence, fall between 438 and 439°C. By comparing the extrapolated trends for kerogens type II and type III to thermally immature samples (i.e., lower than 430°C) from the literature, there appears to be an inflection point in the decreasing activation energy, with decreasing maturity levelling off at approximately 435°C.

Due to a shift toward higher activation energies as thermal maturation progresses, the standard deviation of the activation-energy distributions for each sample also has a positive correlation with  $T_{max}$  values. Similarly to the regression of median activation energies, a distinct trend can be generated for kerogen type II (Figure 7) and a less well-defined trend for type III (Figure 7), with r<sup>2</sup> values of 0.54 and 0.25, respectively.

Based on the regression of median and standard deviation values for different maturities, the median activation energies ( $\bar{E}$ ) and standard deviation ( $\sigma_E$ ) of lower maturity type II (equations 1 and 2) and III (equations 3 and 4) kerogens of the Doig Formation can be determined as a function of  $T_{max}$  according to the following equations:

$$\bar{\mathsf{E}}_{type\,II} = -108.98 + (0.37 \times T_{max}) \tag{1}$$

$$\sigma_{EtypeII} = -38.53 + (0.0930 \times T_{max})$$
(2)

$$\bar{\mathsf{E}}_{\mathsf{type\,III}} = -137.34 + (0.44 \times \mathsf{T}_{\mathsf{max}})$$
 (3)

$$\sigma_{EtypeIII} = -27.14 + (0.0687 \times T_{max})$$
 (4)

Based on the 435°C inflection point in the decreasing trend of the median activation energy with decreasing maturity, median values of activation-energy distributions are deter-



Figure 5. Pre-exponential factor versus median activation-energy crossplot of all samples, and frequency distribution of all activation energies classified by kerogen type.











**Figure 7.** Crossplot of the standard deviation of the activation-energy distributions versus Rock-Eval pyrolysis T<sub>max</sub> of the Doig Formation samples from the study area in northeastern BC and west-central Alberta, showing the trend of decreasing standard deviations toward lower maturity samples. Blue and black dashed lines represent the linear regression for type II and type III kerogens, respectively. Boundaries between generation windows for different kerogen types are after Dow (1977) and Petersen (2003).

mined to be 52 and 54.1 kcal/mol for immature kerogen of types II and III, respectively. Conversely, the standard deviations for immature type II and type III are determined to be 1.93 and 2.75 kcal/mol, respectively. Based on these statistical parameters, synthetic activation-energy Gaussian distributions were created for kerogen types II and III of the Doig Formation (Figure 8).

The wider activation-energy distributions of kerogen type III are not only evident on the discrete activation-energy distribution histograms but can also be observed in the reaction profile generated by the isoconversional kinetic modelling. The isoconversional results are plotted as a single activation energy for conversion rates from 10 to 90% (Figure 9), since the first and last 10% values are often unreliable due to analytical noise in the data (Burnham, 2017). This profile shows that for lower present-day maturity samples, predominant activation energies range from 40 to 58 kcal/mol at 10% conversion. These lower activation energies are associated with samples predominantly of kerogen type III and are likely the product of the breaking of C-O bonds, and possibly C-S bonds. Activation energies at 10% conversion for most lower present-day maturity kerogen type II samples are higher than 50 kcal/mol. At 50% conversion, lower maturity samples have activation energies in the 48 to 60 kcal/mol range. Within this conversion range, bitumen decomposition is probably the cause of the narrower spread and large overlap between activation

energies of kerogen types II and III. At 90% conversion, the high end of activation-energy distributions of type III kerogen causes the spread of dominant activation energies to increase again, ranging from 52 to 90 kcal/mol for low present-day maturities. The results of this study suggest that mixing between kerogen types II and III in the Doig Formation translates into an early hydrocarbon-generation window due to the low activation energies of type III. Furthermore, the kerogen mixing extends the generation process over a broader temperature range due to the combined effect of the lower end of type II activation energies and upper end of those of type III.

## **Ongoing Work**

The work presented here will serve as foundation for a reconstruction of the Doig Formation thermal history through basin modelling. The modelled kerogen activation-energy distributions for different types of kerogen will be used as reaction-kinetics input for the model thermalmaturation simulation, providing reliable source-rock–calibrated parameters, thus decreasing the uncertainty related to timing and type of hydrocarbons generated across the basin.





Figure 8. Histograms of modelled activation-energy distributions of the Doig Formation, northeastern British Columbia and west-central Alberta, based on samples of varying degrees of maturity: **Top**, immature kerogen type II; **Bottom**, immature kerogen type III.

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Figure 9. Kerogen conversion profile, showing reaction progress generated by the isoconversional method.

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