



Kinetics Of Oxidative Degradation – Temp. Based “Energetic” And Subsequently Study Based On, For A Biodegradable Lubricant, By Arrhenious Equation Advancing Its Applicability

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Abstract:

New benchmarks alongwith the time and temperature relationship as has been envisaged through the equation that it demands a certain time period for a biodegradable specie whether a fatty acid or its ester to be come in to the oxidative degradation and compare the test results obtained at different temp.and evaluate changes in chemical reactions.

Assumptions of the pseudo first order kinetics to calculate activation energies in oxidative polymerization of uninhibited 100% oleic triglycerides under thin film oxidation and obtained semiquantitative results from available oxypolymerization data at six temp. from 100°C to 175°C. Several times the TTS superposition has been analysed and co-related the result with that of results found from activation energy using Arrhenious equation. The result showed was that of much accurate. Different stages of oxidative degradation were identified at different temp. and formed a kinetics.

Key words: *Vegetable oils, Oleate, Triglyceriods, Triolein, Unsaturation, Lubricants, Hydraulic Fluids, Biodegradable Oils, Polymerisation, Gelatin, Stability, MicroOxidation, Kinetics*

1.Introduction

Stability of a lubricant is a crucial factor determining the length of drain intervals in actual applications. Since degradation reaction proceed faster at increased temp.,when testing the stability of a lubricant,temperature higher than those in actual application are usually chosen to accelerate testing.Specific test temp may vary or may not be specified in the tests.For example the Baader test(DIN51554,test of susceptibility to ageing according to Baader).is run at 95°C or 110°C, Fed test791C,method 5308.7(Test for corossiveness and oxidation) and oxidative stability of light oils) at 100°C or 250°F,RBOT Tests,ASTM D2112, Oxidation stability of inhibited mineral insulating oil by rotating bomb and ASTM D 2272 oxidation stability of steam turbine oil by rotating bomb at 140°C and 150°C.Many nonstandardized but widely accepted tests such as pressurized differential scanning calorimeter (PDSC) and micro-oxidation,employ a broad range of temp.frequently results obtained fromdifferential tests and temp. are compared.Such data remains confusing or misleadingand always remains a problem for drawing conclusions. Similar problems arise when performance of lubricant at elevated temp. needs to be predicted.Empirical rules are sometimes used to relate the rated egradation to the change in the temp.e.g. that reaction rate doubles with each 10° increase however such approach remains aimless without support of experimental data. In general the Arrhenius equation is employed to compare reaction rates at different temp.,however kinetic mechanisms of the reactions must be known to determine the activation energy and a reaction is needed to establish the reaction order and the rate constants.

On the basis of TTS methodology,the equation can be given as follows—

$$[TTS = t \cdot a^T], \text{ Where}$$

TTS → Time,Temp. Statistics or Energetic.

t → Time of degradation and

aT → Shift factor

In Other Words,We can say thatx

$$[TTS = w \cdot a^T], \text{ Where}$$

w → By WLF equation,a equation constant.

Now the energetic will, take the form of a equation in such a way so as to satisfying and coorelating the Arrhenious equation,as follows -----

[$K = A*(e^{-Ea/RT})$],Where as on solving the equation for two temp. suppose they may be T & T_b

Equation may be written in the form—

[$TTS = t*{e^{-Ea/R*(1/T - 1/T_b)}}$]],Where

T → First Temp.,and

T_b → Baseline Temp.

Now for the condition, [α W β]

We can write two subsequent equations derived from the modified form of Arrhenious Equation.

as,

(1).For the case of ,when T₁= α

The TTS or Energetic can be given as satisfying that very time,temp. relationship accordingly

$$\alpha \Rightarrow [T_1 = t*{e^{-Ea/R(1/T_1 - 1/T_b)}}]$$

&

(2).For the case of ,when T₂= β

$$\beta \Rightarrow [T_2 = t*{e^{-Ea/R(1/T_2 - 1/T_b)}}]$$

T₁ → The temp.before W

T₂ → The temp.comes after W

T_b → Reference Temp.(< 100°C)

Now for a inference if followed by Energetic will follow as or with in the order of range, given by

T₁ < T₂ < 100°C, and this suggests that $\alpha < \beta < 100^\circ\text{C}$.

And for several Imperative conclusions that can be drawn indirectly and listed as

$\alpha < \beta$, $\beta > \alpha$ and also $\alpha, \beta < 100^\circ\text{C}$

Which can be said true on the basis of a natural characteristics

Now from above conclusions, we can say that in general,

$$|T_2| = |T_1|$$

This also suggests a more specific, most probably the true standard and that is

$$\boxed{\alpha W \beta}$$

2. Several Canonical Forms And A Nth Term

Generally the kinetics of the reaction is propagated on the basis of the reaction

$$\boxed{dx/dt = k(t) * f(x)}$$

Where,

$x \rightarrow$ Distribution of component concentrations

$f(x) \rightarrow$ function describing the order

$k(t) \rightarrow$ Rate dependence on temp.

Therefore several and general "ENERGETIC" in the definable form are,

$$T_1 = t * e^{-E_a/R} * (T_1) \text{ ----} \rightarrow (1)$$

$$T_2 = t * e^{-E_a/R} * (T_2) \text{ ----} \rightarrow (2)$$

$$T_3 = t * e^{-E_a/R} * (T_3) \text{ ----} \rightarrow (3)$$

$$| \quad | \quad | \quad | \quad |$$

$$| \quad | \quad | \quad | \quad |$$

$$\boxed{T_n = t * e^{-E_a/R} * (T_n) \text{ ----} \rightarrow (n)}$$

Where Eqn(1), Eqn(2), Eqn(3)---and Eqn(n) are for T_1, T_2, T_3 ---and T_n

Since $k(T)$ is not dependent on conc, whereas $f(x)$ is also not dependent on T , the TTS is applicable not only to the first order kinetics or energetic, but to all the processes which are governed by the $k(t)$. So one expression for TTS or energetic can still be applied for overall reaction as long as the activation energies. Because $k(t)$ describes only the dependence of temp. with the reaction rates, other factors which don't follow the function remain negligible or in other words energetic cannot be followed for the properties such as diffusion, convection, density and viscosity. If we want to understand and study the mechanism for the process such as oxidative degradation of unsaturated materials such as the degradation of biodegradable lubricant such as for the case of oleate, stearate etc, it can be easily done with the help of energetics which will be definite for its applicability.

The degradation is done in the excess of O₂ along with the formation of free radicals and subsequently attack on allylic hydrogen in mono unsaturated fragments ultimately giving rise the formation of peroxy radicals, further steps are exceedingly complex and may involve the hydroperoxide formation and decomposition, peroxy radical addition scission and other acids, and polar materials of approx. the same MW, such as ketones or epoxides, are generated along with oxidative polymerization (oxypolymerization) products of higher MW. Triolein is a suitable material to study oxypolymerization in mono unsaturated media. Cleavage reactions do not significantly affect its MW (890 amu.). Its dimers, trimers and to some extent tetramers can be quantified by size exclusion chromatography. Thin film oxidation can provide excess oxygen and reaction conditions free of diffusion limitations. Changes in convection, volume or viscosity with temperature do not show substantial influence. Therefore, thin film oxidation products of triolein can be analysed and the applicability of TTS to study the process mechanisms can be investigated and compared to the traditional Arrhenius approach.

3. Results & Discussion

All collected oxidation data by triolein oxyreaction shows that no additional effort was made to verify the accuracy and each datapoint in each run but only two methodologies.

- Traditional Arrhenius Approach.
- Alternatively TTS or Energetic Approach.

NOTE :- We use the dependence of reaction rate on time and subsequently the formed products concentrations. Accordingly ----->

3.1. Arrhenius Approach

In Arrhenius approach on different temp. such as 140°C, 150°C, 160°C, 175°C for four hours, 15 min., 1 hour respectively does not decide the linear approach however a fit to be linear approach is shown.

3.2. TTS or Energetic Approach

In the applicability of energetic, we can show that with the use of different time and temp., a most appropriate or plausible approach towards the linear linearity of variables, can be obtained by the use of energetic. Therefore with the help of energetic, it will be true to

obtained the same value of product and hence in other words the activation energy also for a statement congenial to be true from energetic.

4. Other Forms Of Tts Or Energetic

- $TTS = t \cdot 2T - Yb/10 \cdot c.$
- $k(t)/k(Tb) = (nT - Tb)/T.$
- $\ln n/T = Ea/R \times T_2b.$
- $TTS = t \times 4r - rb/25 \cdot c.$

5. Advantages

- (1). Oxy tendencies can be much more clearly depicted with the help of the energetic such as in the micro-oxidation of triolein but remain not stable for other temp. and we don't obtain a linear graph for the several relationships between kinetics and temp. however we will be point out the importance of this energetic in successive dynamism of the other type of reaction involving oxy characteristics. The other types of reactions can be given as- (a). Oxy polymerization (2). Oxidation polymerization
- This energetic can directly be used to tell us the used chemical composition of a material.
- Without calculation with the help of energetic we can infinitely or approximately decide the type and nature of material and feasibility of that material for and to be used in a chemical reaction and thus we can characterize the E_a .
- Any sort of corrections and temp. fluctuations may be considered permitted in the range of applicable temp. & reference temp.

5. Conclusion

Use of energetic in several applications for the case of triolein, vegetable oil, synthetic lubricants and mineral oil can be considered along with the methodologies used in , such as-

- Activation energies can be determined using TTS or energetic with less experimental data or any irregularity in data.

- We can confirm about the reaction rate compared at diff.temp. even the chemical process is unknown.
- The hard to find experimental data for the applicability of the TTS or energetic can be combined linearly to make comparison and prediction.
- At inversion of temp. the TTS or energetic approves its usability and application and therefore aside the use of Arrhenious Equation.
- We will be avoiding the volatility of the substances for the case such as convection, viscosity and therefore also in volume change for the micro-oxidation.

6.Reference

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