



Effects of Temperature on the Reaction Kinetics of the Saponification of Ethyl Acetate

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Introduction

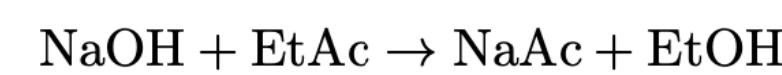
Different reactor designs have different capabilities, offering the users and processes different advantages. The two primary reactor classifications are batch and flow reactors which vary in steady- and unsteady-state conditions. For the purposes of understanding reaction kinetic effects, flow reactors such as the continuous stirred-tank reactor (CSTRs), which allows reactants to be efficiently mixed in a batch-like process while allowing continuous flow through the system, are often used [1,2]. These systems utilize impellers to effectively mix the reagents to form a desired product in a homogeneous reaction, allowing higher reagent concentrations and efficient heat transfer properties. The heat transfer and

calorimetry properties of CSTRs allows for reactions to occur at varied temperatures to maximize reaction rate while maintaining a proper safety temperature control [3]. With the efficient mixing conditions in the CSTRs, the reaction concentration in the tank can be assumed to be the same as the outlet flow of product. With this assumption, the effects of temperature on the saponification reaction of ethyl acetate can be accurately measured and observed while keeping all other variables constant. While current research is often done using a conductometric technique, a classical titration method can be used to analyze the conversion of the resulting product from the hydrolysis of ethyl acetate [2].

Theory

The Reaction

Ethyl acetate (EtAc) reacts with the base sodium hydroxide (NaOH) forming sodium acetate and ethanol in a saponification reaction. The balanced reaction is:

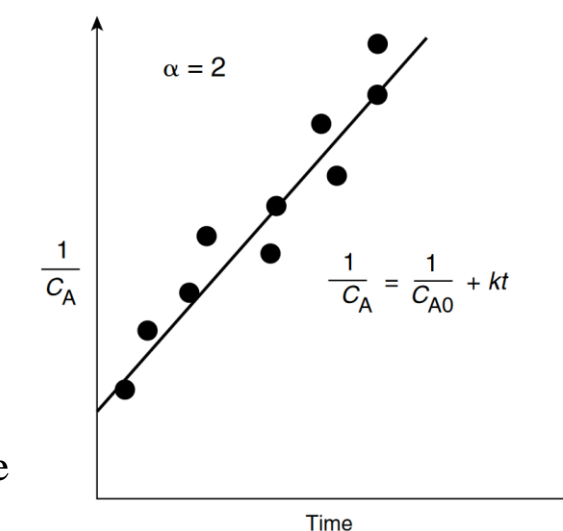


2nd Order Elementary Rate Law

For a reaction with a 1:1 stoichiometric ratio between reactants, and assuming an elementary rate law - the rate of reaction (-r_A) is:

$$-r_A = kC_A^2$$

r_A - generation of species A
k - rate constant
C_A - concentration of A



Additionally, the 2nd Order rate law may be confirmed [4] by finding a strong linear fit when plotting the reciprocal of the reactant concentration against time

Arrhenius Equation – Rate Constant as a Function of Temperature

The Arrhenius equation is used to relate the rate constant to the activation energy and the temperature:

$$k = A \exp\left(\frac{-E_A}{RT}\right)$$

A - constant
E_A - activation energy
R - gas constant
T - absolute temperature

Conversion – Dependencies on Flowrate & Temperature

Conversion is a measure of how much reactant has been turned into product in a chemical reaction, expressed as a percentage.

This model predicts that a higher absolute temperature will result in a higher rate constant, and thus a faster reaction. Two more parameters are needed to find the rate constant from experimental data: conversion and residence time. Conversion is calculated by:

$$X = 1 - \frac{\text{molar flow at effluent}}{\text{molar flow into reactor}} = 1 - \frac{F_{\text{NaOH, out}}}{F_{\text{NaOH, in}}} = 1 - \frac{C_{\text{NaOH, out}} * \dot{V}_{\text{out}}}{C_{\text{NaOH, in}} * \dot{V}_{\text{in}}}$$

As the conversion is dependent on concentration and flowrate, and the concentration at a given time has a dependency on temperature, conversion is expected to increase with increasing temperature or flowrate.

Objectives

Objective 1

- Determine the conversion of NaOH as a function of time across multiple temperature trials to confirm conversion temperature dependency

Objective 2

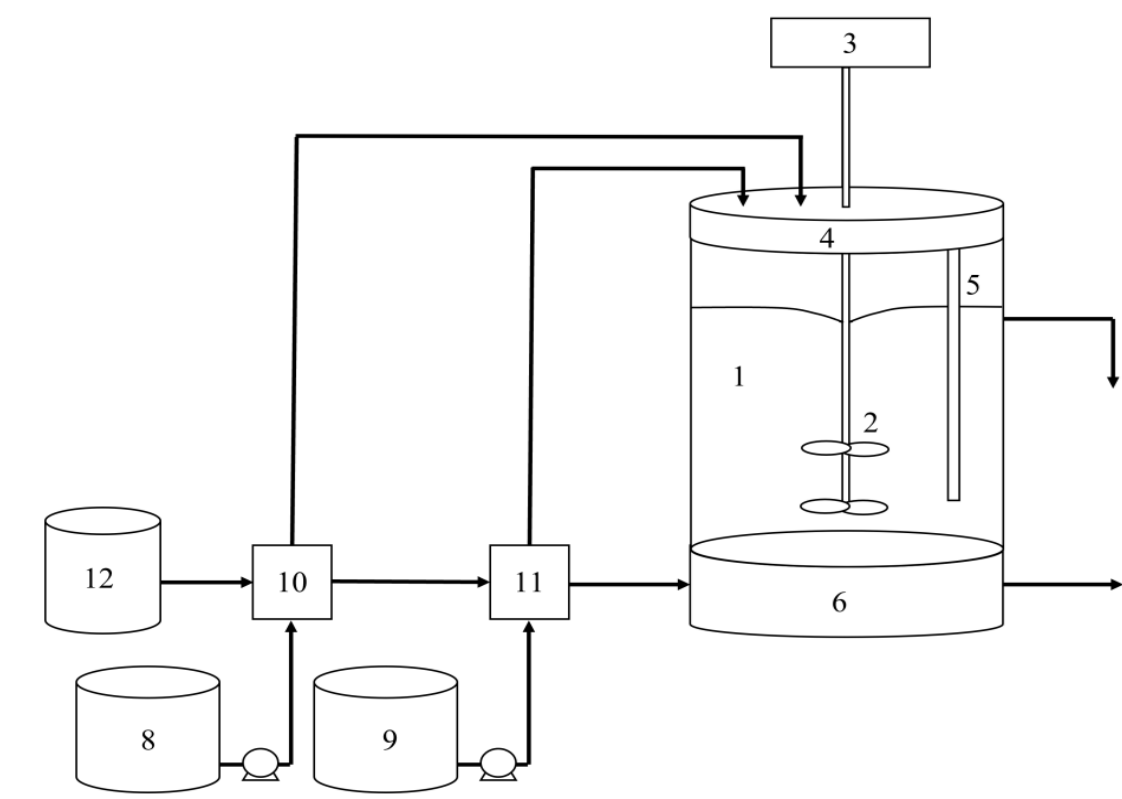
- Show an increasing reaction rate constant with increasing temperature, following the Arrhenius's equation

Objective 3

- Support that the saponification of ethyl acetate follows an elementary rate law

Methods

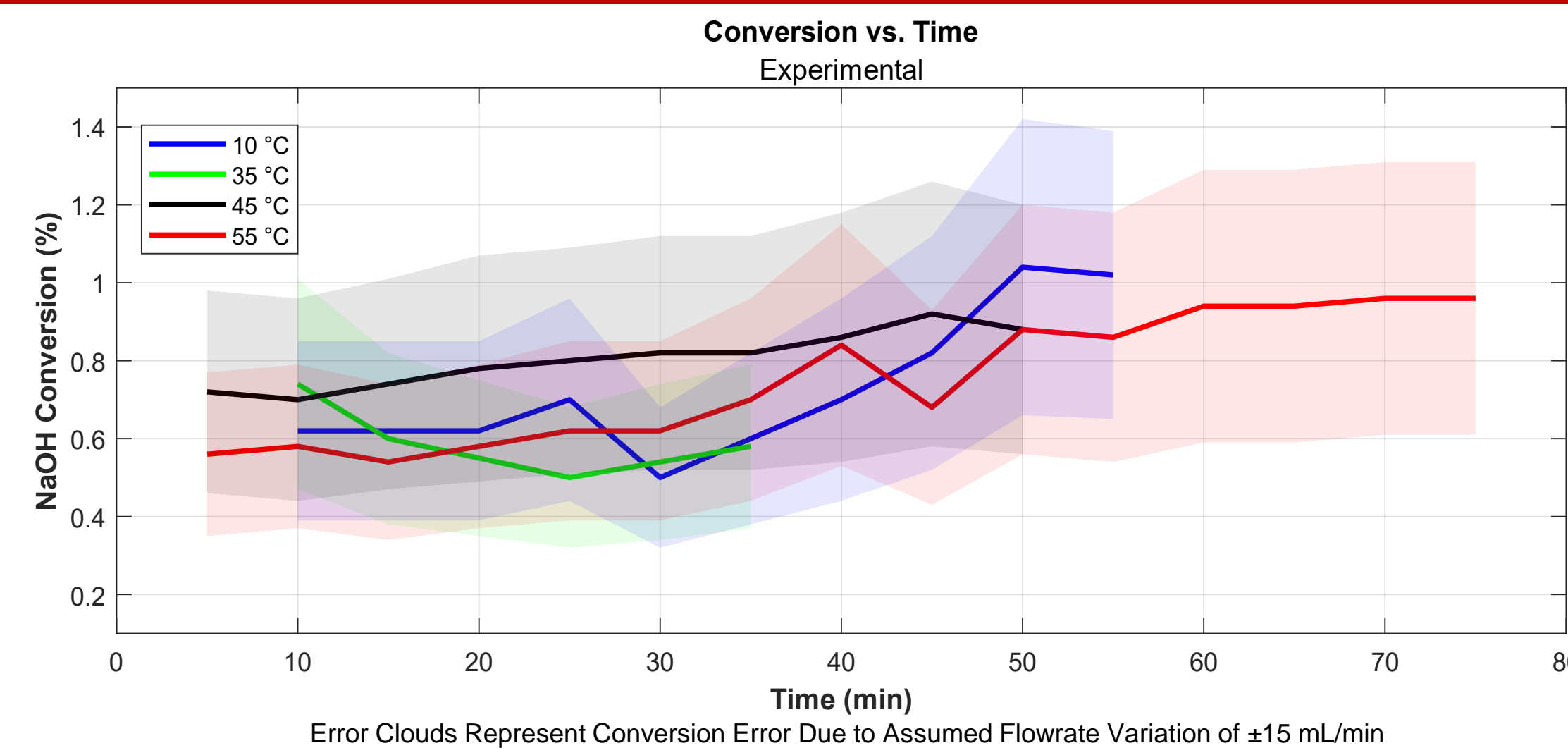
Solutions of hydrochloric acid, ethyl acetate, and sodium hydroxide were prepared, all with concentrations of 0.1 M. A peristaltic pump and tuning knobs on two fickle flow meters were used to feed 50 mL/min of ethyl acetate solution and 50 mL/min of sodium hydroxide solution into the CSTR. Temperature was manipulated using a water bath which was set to 10, 35, 45, and 55 degrees Celsius between trials. Paper towels were put into ice and wrapped around the tank to cool it more quickly in the 10 C trial. 10 mL samples of effluent were taken every five minutes and neutralized by quenching with 10 mL of a hydrochloric acid solution. This was titrated with sodium hydroxide solution and 3 drops of phenolphthalein was used as the indicator. Sample sodium hydroxide concentrations were obtained from the known titrated volumes.



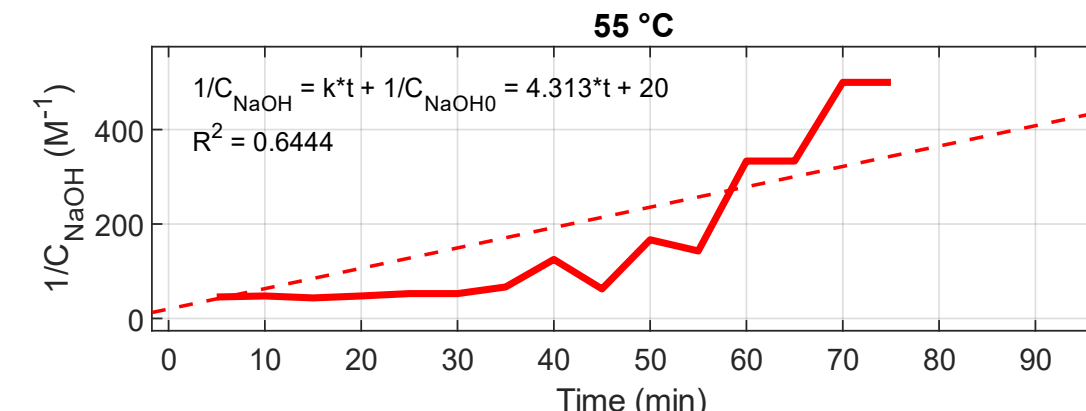
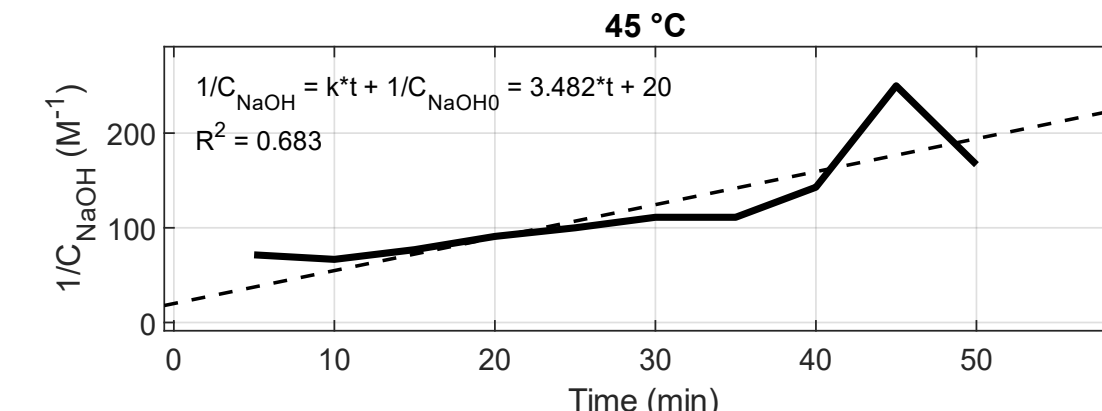
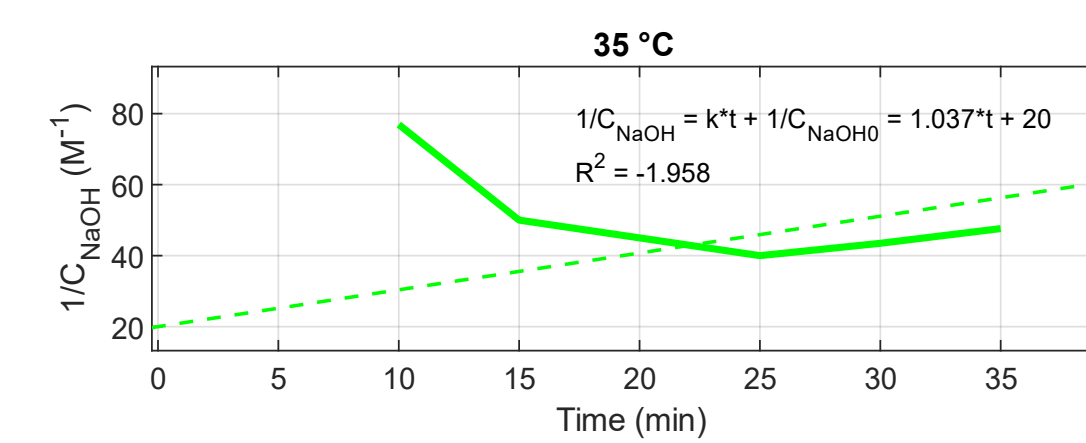
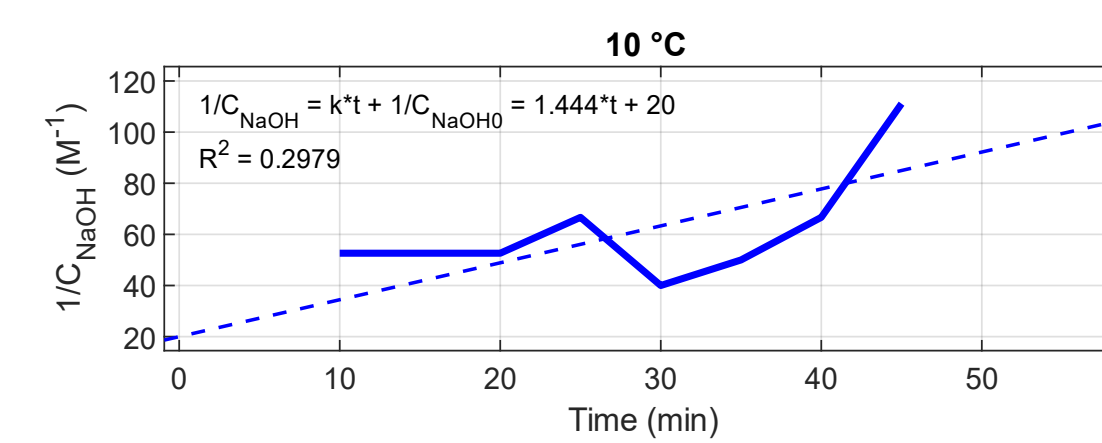
- CSTR
- Impeller
- Impeller interface
- Water bath
- Effluent (100 mL/min)
- Ethyl Acetate Reservoir
- NaOH Reservoir
- Ethyl Acetate Flowmeter (50 mL/min)
- NaOH Flowmeter (50 mL/min)
- Water bath reservoir

Results

Conversion



Rate Constant & Rate Order Determination



Discussion

There were large errors in the data. The combined use of a finicky peristaltic pump with a flowmeter resulted in a pulsing rather than continuous flow. Throughout the course of the reaction's progression, the flowmeters were found to randomly stabilize or oscillate between no flow to as high as 80 mL/min. This prevented the collection of precise data.

Discussion – Objective 1

The conversion did not show any consistent dependency on temperature, but it did increase with time for all trials as expected. This was attributed to the faulty flow measurements, where an assumed error of ±15 mL/min in the flow rates was plotted as an error cloud centered about the conversion measurements. Given that a higher flowrate variability was observed in practice, it can likely be concluded that the conversion data is not of practical value.

Discussion – Objective 2

An increasing reaction rate constant was observed with increasing temperature, (excluding the 35 degree trial whose correlation coefficient would support that it cannot be represented well by a linear fit). From the linear regression taken for an assumed 2nd order reaction plot, the reaction rate constant was taken to be the slope. The rates found were 1.444, 3.482, and 4.312 M/s for the 10, 45, and 55 degree trials respectively. This was in line with the theoretical trends provided by the Arrhenius equation. Though the poorness of the linear fit may indicate that these values are likely too deviate significantly from the true values with more accurate flowrates.

Discussion – Objective 3

The saponification of ethyl acetate by sodium hydroxide is expected to follow an elementary rate law. Owing to the 1:1 stoichiometric ratio between the reactants, this implies a 2nd-order reaction. The data obtained does not support this experimentally, most likely due to the inability of the apparatus to allow for proper control over volumetric flow rates of the reactants in the CSTR. The low correlation coefficient values for the linear fits do not support expectations.

Design Extension

Saponification of ethyl acetate by sodium hydroxide has applications in several industrial processes such as soap making, and production of food preservatives and biofuel feedstock. For successful operation and optimal performance of this reaction within a CSTR, the following design considerations must be taken into account: reactant flow rate, reactor sizing, reaction kinetics and mixing.

Reducing the flowrate of the reactants will result in a higher conversion due to the increased residence time, but this will sacrifice the overall throughput. A larger reactor will increase the overall residence time, thereby increasing the conversion rate. Thus, increasing the reactor vessel volume will increase production rates without compromising effluent quality. A vessel's impeller design and speed must ensure adequate mixing for heat and mass transfer. Additionally, the impeller speed should be selected carefully to minimize utility costs.

Conclusions

The experimental results provided little discernible correspondence to theoretical expectations. The reaction rate constant was expected to increase as a function of temperature, and the reaction was expected to be 2nd-order following an elementary rate law, although only the former of these expectations could be somewhat experimentally evidenced. The conversion data was not viable. While other measurement inconsistencies may have been present, the inability to properly control the volumetric flowrates of the reactants to an acceptable extent led to mostly nonviable experimental data. This obviated the possibility of obtaining precise measurements of the reaction rate constant, conversion, or proper determination of the reaction order, underscoring the need for the Chemical & Biomolecular Engineering department to purchase higher quality experimental apparatuses for future students to make better determinations.

Acknowledgements

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References

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