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STUDIES ON THE TECHNIQUES, KINETICS AND THERMODYNAMICS OF CORN OIL EXTRACTION: MINI REVIEW

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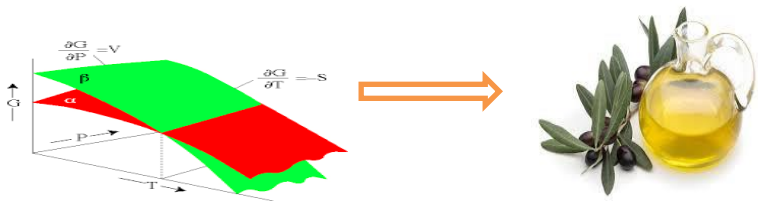
ABSTRACT



Corn oil contains about 58g of polyunsaturated fatty acids per 100g of oil and these polyunsaturated fatty acids which are essential to the human body helps maintain healthy blood vessels, nerves and tissues. Oil extraction from corn has traditionally been carried out on the whole grain using such methods as solvent extraction, mechanical pressing and recently supercritical CO_2 extraction. In this mini review, this potential reveals the techniques, kinetics and thermodynamics of corn oil extraction. Here, authors review contemporary advancement in the health importance of corn oil, different techniques of corn oil extractions and the kinetics and thermodynamics of corn oil extraction. The present study gives an account of full knowledge of the use of the outstanding kinetics and thermodynamics of corn oil extraction.

Keywords: Kinetics and thermodynamics, Corn Oil Extraction, Zea maize, Pharmacological Values.

INTRODUCTION

Oilseeds are the major source for the production of edible oils that are regarded as important components of diet, an important source of energy, essential fatty acid such a linoleic acid and other fat soluble vitamins such as vitamin A and vitamin D. Corn is a small hard seed obtained from a cereal grass which is mostly used as food and livestock fodder(Connor et al.,

1992; Darkwah et al., 2018). It is a worldwide staple and in Asia and Africa specifically, Ghana for instance, corn is popularly known for its use in preparation of food like banku, kenkey, porridge," nkyekyere" and "tuo-zaafi". Corn is also used for numerous industrial products, in distillation and fermentation industries and for the production of starch and corn syrup. It ranks with wheat and rice as one of the largest crops grown in Ghana. Corn is composed of about 2.9% crude fibre,10% fibre,10% protein,4.3% fat,1.5% ash,9% cell wall and 71.7% carbohydrate(Kumar and Jhariya, 2013). Corn oil is a pale-yellow drying or semi-drying edible oil extracted from germ of corn and used for cooking and salad preparation and this oil is finding wide applications at home, restaurant, hotels, hospitals and other food industries. Corn contains about 4% of oil and it is mostly obtained from the germ of the corn. The corn germ contains about 85% of the oil and 80% of the minerals present in the whole germ (Olutoye and Garba, 2008). The oil extracted from corn has several desirable properties, including its mild nutty flavor, high levels of unsaturated fatty acids, low level of saturated fatty acids and high level of tocopherol (Kumar and Jhariya, 2013). Corn oil contains about 58g of polyunsaturated fatty acids per 100g of oil and these polyunsaturated fatty acids which are essential to the human body helps maintain healthy blood vessels, nerves and tissues. Actually, various techniques such as mechanical extraction, solvent extraction and super critical fluid extraction are used to obtain oil from corn.

The solvent extraction has become the most popular because of its high percentage of oil yield from seeds. Also, hexane I often used due to its lower boiling point, for easy separation after extraction; its non-polar makes it suitable for extracting corn oil which is also non-polar and its comparatively low toxicity when compared to other solvents (Nwabanne, 2012). Several parameters such ass particle size, volume of solvent used, the structural and mechanical properties of the oilseed after a thermal treatment and milling before preparation of the material for extraction. During the extraction itself, the most important conditions are the temperature and duration of the extraction, as well as the polarity of the solvent used for extraction.

The rate of extraction of corn oil is temperature –dependent, the enthalpy and entropy are positive implying that the reaction is endothermic and irreversible respectively while the Gibbs free energy is negative which means that the reaction is feasible.
Corn is widely consumed by the people, however not much work has been done on extraction of oil from corn. In this mini review, we mainly concentrated on the most contemporary advances on the kinetic and thermodynamic factors on extraction of corn oil, since there exists limited study in literature.

REVIEW

Zea mais

Corn is one of the chief grains in the world apart from wheat and rice. Corn is almost grown worldwide and used mostly as food (Orthoefer, 1987). The two main food substances obtained from corn is the flour and oil which is mostly confined in the germ of the corn (Moreau et al., 2002). Apart from its use as food, it is used to produce ethanol and also through enzymatic activities is used to produce high fructose syrup. Corn is from the cereal family and has several varieties which are based on the several factors like time taken to mature, length of the corn crop, the number of corn seeds in a row and many others. Some varieties include Obatanpa (Figure 1) which is a very common variety in Ghana, dent corn, flint corn, sweet corn, pod corn, Indian corn etc.

Figure 1. Diagram showing a typical *Zea mais*

Uses of Corn Oil

Corn oil is a yellow golden liquid with a pleasant mild taste and it is obtained from corn kernel, fibre and germ. It is used as cooking oil for frying foods because it doesn't smoke or discolor. It is also used in the manufacturing of spreads and margarines(Stolp and Stute, 1982). Apart from its use as food, it is also used in the manufacturing of cosmetic or beauty products such as skin and hair pomades, nourishing lip balm, soaps, hand creams and many others (Olutoye and Garba, 2008). Also, it is used in pharmaceuticals preparations to produce drugs (figure 7).

Figure 2. Diagram showing oil extracted from corn

Health / Pharmacological Benefits of Corn Oil

Corn oil is a rich source of omega -3 and omega-6 fatty acids (figure 2), also called linoleic acids, which cannot be synthesized by the body but these fatty acids enable various functions in the body which result in the normal growth and development the body.

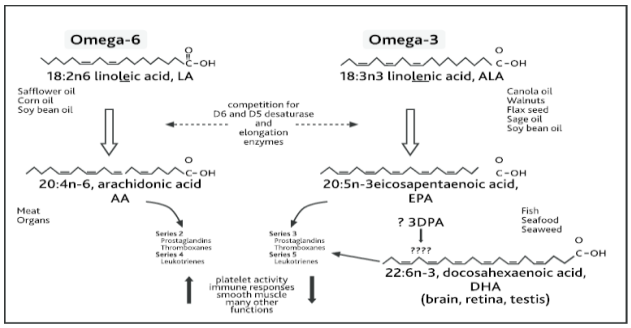


Figure 3: schematic diagram of omega -3 and omega-6 fatty acids.

These essential fatty acids sustain optimal performance of the brain, regulate reproductive function and enhance bone health (Rhee et al., 1972; Eka, 1980; Yeboah & Darkwah., 2017; Darkwah et al., 2018). They also relief the pain associated with rheumatoid arthritis. Research also shows that essential fatty acids play a role in skin health since they help manage eczema and acne. Transmission of nerve impulses is also facilitated by essential fatty acids (Connor et al., 1992).

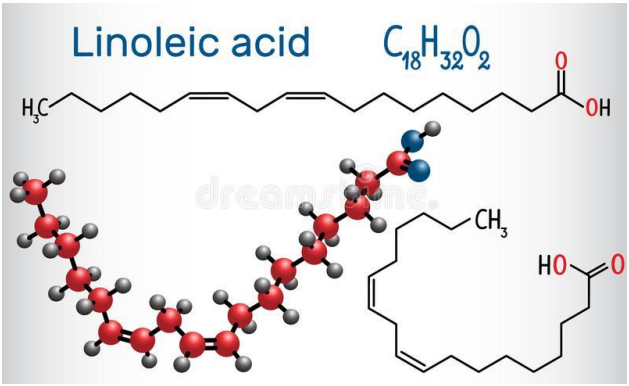


Figure 4. Schematic diagram of linoleic acids in corn oil

Research studies have also established a close relationship between essential fatty acids and improved cardiovascular health in that they reduce bad cholesterol in the blood and improve good cholesterol levels which in turn normalize blood pressure and this bears a positive effect on heart health, hence reducing the risk of heart disease and even stroke.

Table1. Selected phytochemicals obtained from oil corn and their pharmacological / health values.

Phytochemicals	**Therapeutics**
1. Essential fatty acids	i. Optimal performance of the brain, regulate reproductive function and enhance bone health (Rhee et al., 1972). ii. Help in treating pains associated with rheumatoid arthritis, iii. This helps in dermatology disease therapy.
2. Phytosterol	i. Have the capacity to lower blood cholesterol, therefore decreases the chances of risk of cardiovascular disease and related. ii. Prevention of breast, colon and prostate cancers and used in cancer therapy.
3. Tocopherols / vitamin E	i. Sustain metabolism and boost immune system. ii. Inhibit the formation of carcinogens in the stomach. iii. Help to prevent the growth of cataracts in the eyes.

Phytosterol (figure 5), also known as plant sterol is also found in corn oil in high percentage and these compounds also have the capacity to lower blood cholesterol by inhibiting the absorption of cholesterol in the intestines, hence reducing the risk of cardiovascular disease and stroke as well(Moreau et al., 2002; Koomson et al., 2018).

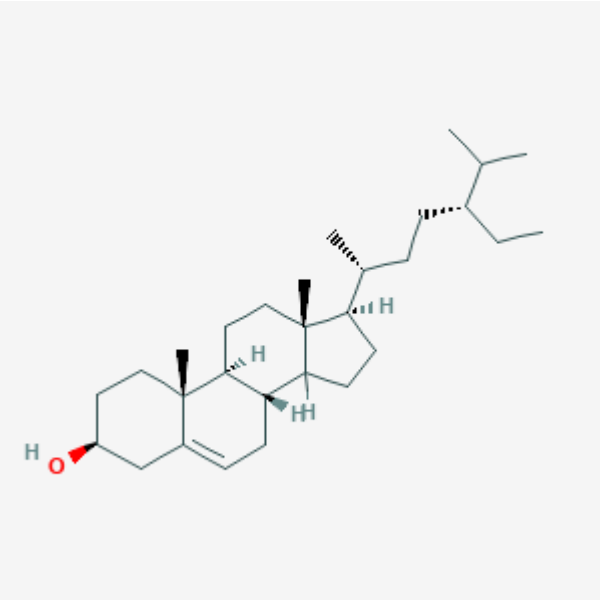


Figure 5. Schematic diagram of the chemical structure of phytosterol

Phytosterols also are beneficial in prevention of breast, colon and prostate cancers because they inhibit the growth of tumors. Also, corn oil is noted for its level of tocopherol (figure 6). Tocopherols belong to the vitamin E family and they have a lot of antioxidant activity and these nutrients protect cell from harmful effects of free radicals.

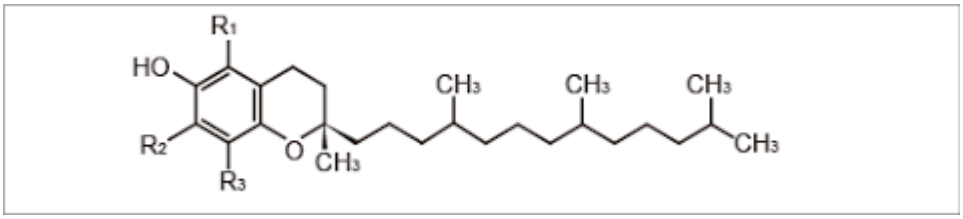


Figure 6. Schematic diagram of the chemical structure of tocopherol

Tocopherols sustain metabolism and boost immune system. They inhibit the formation of carcinogens in the stomach and also help to prevent the growth of cataracts in the eyes and help to improve lens clarity(Connor et al., 1992) .

Figure 7. Diagram showing drugs obtained from corn oil for health benefits.

Corn Oil Extraction Techniques

Corn oil can be obtained from the fiber, corn kernel and the corn germ but of all the three, the corn germ is the oil-rich center, in that it contains about 80 to 85% of oil of the whole corn grain(Moreau, 2005; Adayeh et al. 1998). Several methods are used to obtain oil from corn(Singh et al., 2002; adeeko & Ayibola, 1990; Amoo et al., 2004; Gandhi et al., 2003). Some of which including the wet milling process, (figure 8) the sequential extraction process(SEP), aqueous enzymatic process and (Fellows, 1996; Goodrum &Kilgo, 1987)solvent extraction (figure 9) which is the most common process used by industries to obtain oil from corn, because its less expensive, less toxic and yields more amount of oil. There also are several systems for removing oil from oilseeds, including the wet process, the dry process, and solvent extractions. The kinetics of oil extraction from oilseeds, corn oil and by-products from industries which use corn is dependent on a number of factors (Mattil et al., 1964; Sergeev et al., 1974). These factors include the composition and morphology of the raw material, and the structural and mechanical properties of the flakes after hydrothermal treatment and milling before preparation of the material for extraction (Leibovitz & Ruckenstein et al., 1983; Karlovic et al., 1988; Karlovic et al., 1989; Minasyan et al., 1972). Throughout the extraction, the supreme significant conditions are the temperature and duration of the extraction(Hickox, 1953), as well as the polarity of the solvent used for extraction (Arnold et al., 1956; Gulbaran E. & Gulbaran S.H., 1981; Becker, 1978).

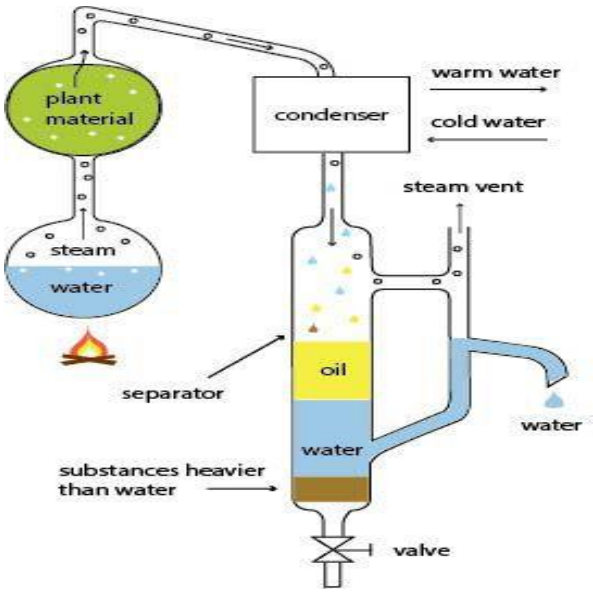


Figure 8. Schematic diagram showing the extraction process of oil from corn.

Karlovic and group also studied the temperature and moisture content effect on the kinetics of oil extraction from corn germ flakes prepared by a dry degermination process.

For numerous decades, commercial-grade hexane has been adopted as the solvent of choice for the extraction of most oil from corn oil. The solvent that is mostly used is n-hexane because it's less expensive, less toxic and more polar (Nwabanne, 2012; Mezaine, 2006). Other solvents used in place of hexane (figure 9) are petroleum ether and ethanol (Moreau and Hicks, 2005; Franco et al., 2007; Abraham et al., 1993).

Rao et al. and Hassanen studied extraction of oilseed model systems with alcohols, and showed that when the moisture level in flakes was below 3%, aqueous ethanol was an effective extraction solvent (Rao et al., 1958; Hassanen, 1985). Aqueous ethanol with a tribasic acid, such as phosphoric or citric, was used as an alternative solvent to hexane for the extraction of glanded cottonseed by Hron et al. and Wan et al. found alternative hydrocarbon solvents for cottonseed extraction and they recommended 2 hydrocarbon solvents, heptane and isohexane, as potential replacements for hexane (Hron et al., 1992; Wan et al., 1995; Johson & Lusas et al., 1983).

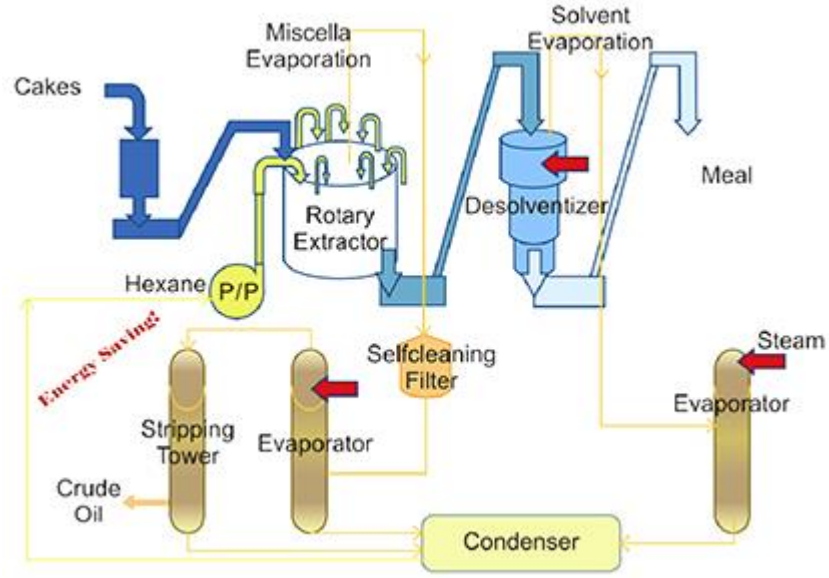


Figure 9. Schematic diagram showing the industrial extraction system of oil extracted from corn using solvent extraction technique

Proctor and Bowen also compared Hexane and isopropanol as solvents for use in ambient-temperature equilibrium extraction of rice bran oil (Proctor and Bowen, 1996; Karnofsky 1981). Oil extraction by ethanol from partly defatted surged sunflower seeds in pulsed and nonplused extractors was compared by Sineiro and group in 1998 (Sineiro et al., 1998). Ibemesi and Attah extracted the seeds of rubber [*Hevea brasiliensis* (Kuth) Muell. Arg.] and melon (Colocynthis vulgaris Schrad) using different solvents at various temperatures, and these two Researchers also determined the temperature coefficients and enthalpy changes associated with the extraction process. They achieved Enthalpy change values within the range 4 - 13.5 $kJmol^{-1}$ (Ibemesi and Attah., 1990).

Kinetic and Thermodynamics of Corn Oil Extraction

Most kinetic and thermodynamic studies show that, the rate and the rate reaction constant are temperature dependent (figure 10). An increasing temperature with a decreasing extraction constant implies that the reaction is slow and also an increasing temperature with an increasing extraction constant means that the reaction occurs at a faster rate(Nwabanne, 2012, TOPALLAR and GEÇGEL, 2000; Ekey, 1954; AOAC, 1990).

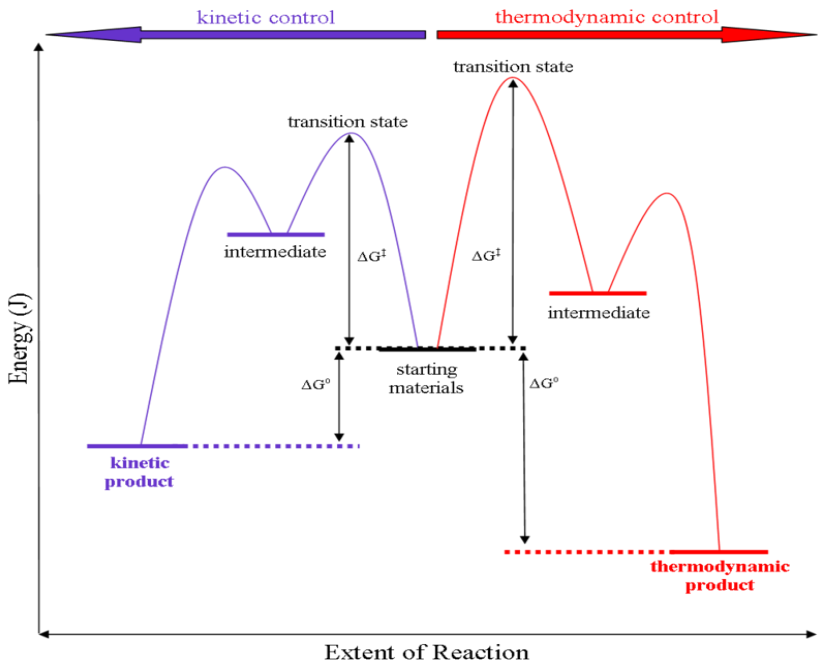


Figure 10. Schematic diagram showing Kinetic and Thermodynamic properties

Activation energy on the other hand, which also is rate and temperature-dependent also a kinetic parameter represents the minimum amount of energy that a reactant requires to proceed to the formation of products (figure 11). Research shows that positive activation energy infers that the reaction occurred at a slower rate and vice versa (Sayyar et al., 2009).

Table 2. Selected thermodynamic parameters and their differences

Thermodynamic parameters	Relationships
1. Enthalpy	i. The amount of energy possessed by a thermodynamic system for transfer between itself and its environment ii. A positive enthalpy value means the reaction or extraction of oil is endothermic while a negative enthalpy value means the process of extraction of oil is exothermic.
1. Entropy	i. Measures the randomness of a reaction ii. Positive entropy value obtained for entropy means that the reaction is very random and irreversible (figure

	10), while a negative entropy value indicates that the reaction is not random and easily reversible (Meziane and Kadi, 2008).
2. Gibbs free energy	i. Determines the spontaneity and feasibility of a reaction. ii. A negative Gibbs free energy value means that a reaction is spontaneous while a positive Gibbs free energy means that the reaction is not spontaneous.

The thermodynamic parameters which include the enthalpy, entropy and the Gibbs free energy also influence the occurrence of a reaction (table 2). Enthalpy represents the amount of energy possessed by a thermodynamic system for transfer between itself and its environment (Adeib et al., 2010).

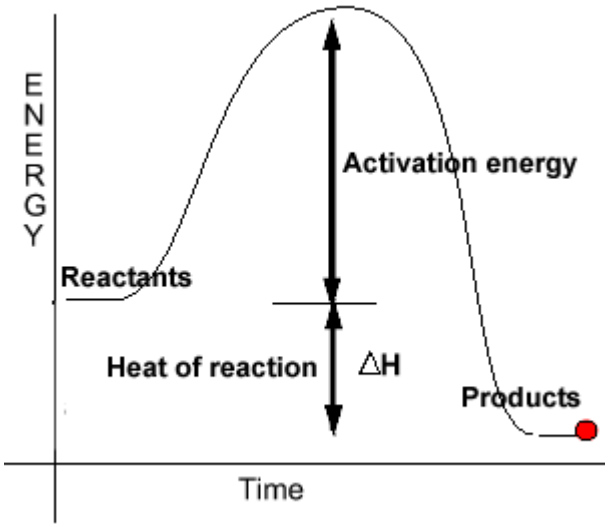


Figure 11. Schematic diagram showing Activation Energy

A positive enthalpy value means the reaction or extraction of oil is endothermic in that energy has been transferred from the environment to the system while a negative enthalpy value means the process of extraction of oil is exothermic, which means that work has been done by the system through the transfer of energy to its surrounding (Liauw et al., 2008).

Entropy measures the randomness of a reaction, a positive entropy value obtained for entropy means that the reaction is very random and irreversible (figure 12), while a negative entropy value indicates that the reaction is not random and easily reversible or means that the reaction is very stable (Meziane and Kadi, 2008). The Gibbs free energy determines the spontaneity and feasibility of a reaction. A negative Gibbs free energy value means that a reaction is spontaneous in that the reaction can occur without any external factors and feasible while a positive Gibbs free energy means that the reaction is not spontaneous and feasible.

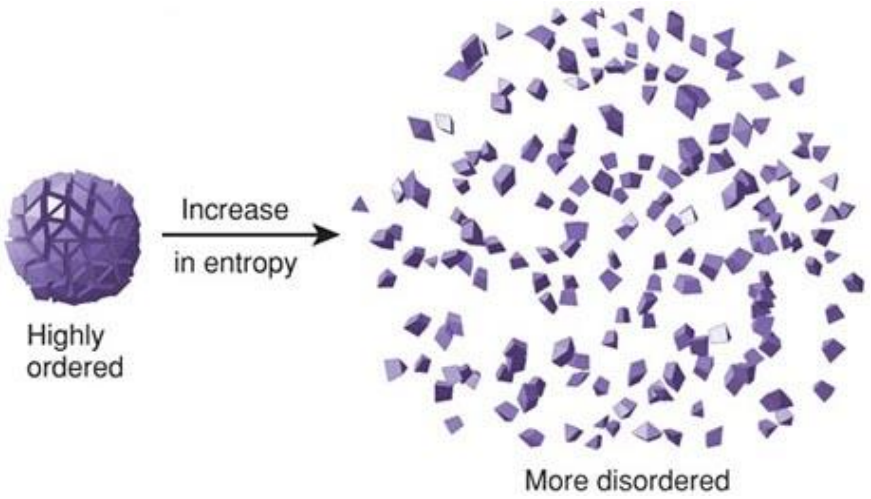


Figure 12. Schematic diagram showing Entropy of molecules

Most kinetic and thermodynamic studies on oil extraction also reveal that the rate is temperature and time-dependent and also the extraction process is endothermic (figure 10), irreversible and spontaneous. (Sayyar et al., 2009, TOPALLAR and GEÇGEL, 2000; Kosti et al., 2014; Amarante er al., 2014) who worked on thermodynamic and kinetic studies of oil extraction from oilseed reported that the rate is temperature dependent and also the extraction of oil is endothermic, irreversible /random and spontaneous (Table 3).

Table 3. Comparisons between Kinetic and thermodynamic, and Activation energy in oil extraction

Mechanisms	Comparisons
1. Kinetic and thermodynamic	a. The rate and the rate reaction constant are temperature dependent b. Increasing temperature with a decreasing extraction constant. c. Increasing temperature with an increasing extraction constant d. The extraction process is endothermic e. The reaction is irreversible /random and spontaneous.
2. Activation energy	a. Reaction rate and temperature are dependent. b. Positive activation energy infers that the reaction occurred at a slower rate and vice versa (Sayyar et al., 2009)

CONCLUSION

In conclusion, this mini review highlights the most recent advances on the kinetics and thermodynamic of corn oil extraction. This review has added onto knowledge available on the mechanisms used in the extraction of corn oil, which ultimately would help research scientists to identify more kinetic targets and develop alternative advanced extraction method interventions. It is also expected to serve as a valuable source of information for scientist that

would enlighten them in understanding the need to adhere to practices and to employ an alternative procedure that is free of such challenges and cost effective to corn oil extraction. Therefore, there is little uncertainty that the massive advancement of corn oil will endure to develop in the near future. In view of that, more studies are also needed to making full use of the exceptional kinetic and thermodynamics of corn oil extraction techniques.

Conflict of interest statement

The Authors declare that they have no conflict of interest.

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