

*Full Length Research Paper*

# Temperature effects on iodine catalysed dimerization of fluted pumpkin (*Telfairia occidentalis*) seed oil

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**In this work the effects of temperature on the dimerization of pumpkin seed (*Telfairia occidentalis*) oil was investigated and the dependence of dimer yields on reaction temperature and time was determined. Pumpkin seed oil (2283.75 g) was solvent extracted from seeds of the fluted pumpkin (*Telfairia occidentalis*), using petroleum ether (60 to 80°C). Samples of the oil were dimerized at varying temperatures ranging from 310 to 350°C; using 0.25% weight resublimed iodine catalyst under nitrogen atmosphere. The extent of reaction was determined by measuring changes in refractive index, molecular weight and acid values of the dimerized oil samples. A dimer yield of 18.7% was obtained in the process whose progress was a function of temperature and reaction time. Thermodynamic investigation showed that the reaction was exothermic.**

**Key words:** *Telfairia occidentalis*, dimerized oil, dimer, exothermicity, reaction order, kinetics.

## INTRODUCTION

The quest for industrial raw materials based on natural renewable resources which can serve as an alternative to petroleum, has been of interest to many researchers in recent times. Vegetable oils such as soybean oil, tall oil and safflower oil, among others, are increasingly being used as such alternatives. These plants have numerous intermediates like dimer fatty acids which find application in the manufacture of coatings, adhesives, printing inks, cosmetics, etc. Dimer acids are dibasic acids derived from thermal or catalytic polymerization reactions of the simple monohydric esters of drying or semi-drying oils. They are predominantly C36 dicarboxylic acids with small fraction of monocarboxylic acids and some C54 tricarboxylic acids (Breuer, 1979; Parker, 1965). Dimerization of vegetable oleic acid or tall oil fatty acid (TOFA) yields dimer acids, originally introduced in the 1950s by General Mills Chemicals and Emery (now Cognis Corp.). It is a complex reaction that generally gives a mixture of aliphatic branched and cyclic C36 – diacids (dimer acid) as the main product, apart from trimer acids and higher condensed polymer acids as

well as other products such as isostearic acid, unreacted oleic and stearic acids (Hill, 2000).

In a study carried out using infrared (IR) spectrophotometry to determine the isomerization of linseed oil during its polymerization, it was established that the formation of trans-isomers enhanced the polymerization reaction (Helme and Molines, 1957). Subsequently, Cecehi et al. (1986) showed that dimer structures and the mechanism of its production could be a function of the method of its formation. They obtained methyl linoleate dimer through thermal and thermocatalytic polymerization using ruthenium catalyst and confirmed two structures, cyclic (mono- and bi-), and aliphatic structures, respectively, for the two different production routes. High molecular weight soybean oil polymers were isolated by Tao et al. (2001), using distillation and mass spectrometric analysis and it was observed that they were dimers formed by Diels-Alder reaction. An earlier work by Kikawa et al (1997) showed that, a low temperature process (50 to 200°C) involving the use of activated clay and oxygen/nitrogen mixture was used to dimerize purified and crude unsaturated fatty acids. Anyaogu et al. (2010) as well as Boot and Speek (1994) have reported the optimum condition for the polymerization of soybean oil to include 350°C, 0.0025% iodine catalyst and a

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reaction time of 20 min under inert atmosphere.

The fatty acid precursors used for the dimerization and oligomerization are generally tall oil, soybean oil and rapeseed oil or dehydrated castor oil. The diversification of the sources of precursors for the production of dimer acids will reduce pressure on the aforementioned oils which are already in use in many domestic and industrial applications. It is in this light, that a locally available alternative in Nigeria, namely, pumpkin seed oil fatty acid, obtainable from *Telfairia occidentalis* seed oil was used. Furthermore, the choice of pumpkin seed oil as a fatty acid feedstock was based on the fact that it contains fatty acids of oleic and linoleic (about 63%), and a high degree of unsaturation, hence its drying properties (Asiegbu, 1987).

This work is a report on the dimerizability of pumpkin seed oil (PSO), using iodine catalyst to establish the optimum reaction conditions and obtain some thermodynamic data on the dimerization process (Boot and Speek, 1994).

## MATERIALS AND METHODS

Pumpkin seed oil (PSO), was solvent extracted from seeds (obtained at the Ibagwa market, near Nsukka, Enugu State, Nigeria), using low boiling petroleum ether (60 to 80°C). The oil extract was water degummed and alkali refined.

Modified methods of Boot and Speek (1994) and Anyaogu et al. (2010) were used for dimerization of pumpkin seed oil. The degummed pumpkin seed oil (200 g) was poured into a reaction kettle, followed by the addition of 0.005 g of resublimed iodine. A steady stream of nitrogen gas was introduced while stirring, and the reaction kettle was heated to and held at 300°C for 40 min. Samples of the reaction mixture were collected periodically and stored for further characterization. This reaction procedure was repeated at 310, 320, 330, 340 and 350°C, respectively.

Dimer yield was determined by preparative thin layer chromatography using a mixture of solvents consisting of n-hexane, diethyl ether and glacial acetic acid in the ratio 7: 2.9: 1. Both the extracted and the dimerized PSO samples were characterized using ASTM and AOCS methods (Anyaogu, 2010). The following physicochemical properties were determined: acid value (neutral solution method), saponification value, specific gravity, refractive index (using Abbe refractometer, Bellingham and Stanley Ltd A82316), iodine value (Wij's method), molecular weight (cryoscopic method) and colour (Gardner).

## RESULTS AND DISCUSSION

An oil yield of 43% was obtained from the seed sample of *T. occidentalis* (fluted pumpkin) used. The yield falls within the range of 33 to 47% reported by Asiegbu (1987) and Attah and Ibemesi (1990).

The physicochemical properties of the PSO used are as follows: refractive index (1.4725), Gardner Colour (4), saponification value (200), iodine value (119), relative density or specific gravity (0.913) and acid number (3.0) (Ucciani, 2000).

The values of the molecular weight of dimerized oil

samples withdrawn at 5 min interval, from iodine catalyzed dimerization of PSO, as determined by cryoscopy, were plotted as a function of time and temperature in Figures 1 and 2, respectively. It can be seen from these graphs that the molecular weight is generally a function of time and temperature, ranging from 450 g/mol (0 min, 300°C) to 1040 g/mol (40 min, 350°C). Beyond this, no further significant molecular weight increase was observed as shown in Figures 3 and 4, plotted to highlight this observation. This could be due to a number of factors, such as formation of monomeric fatty acid groups, intramolecular dimerization with attendant ring formation, but without any change in molecular weight, etc. This explanation corroborates the result of an earlier work by Bradley (1938).

Similar plots were obtained by Kyenge (2006) in the dimerization of pumpkin seed oil using sulphur catalyst. In his study, however, higher molecular weight values (over 17,000) were obtained, which could be attributed to better catalytic activity of sulphur. Also, similar trends were observed by Egbo (2006) and Uwakwe (2006) in the dimerization of melon seed oil (MSO) using iodine and NaHSO<sub>4</sub> catalyst systems, respectively. Increase in the refractive indices of dimerizing oil samples were also observed and are plotted as a function of time and temperature in Figures 5 and 6 respectively.

Figure 5 revealed that refractive index increases with time of dimerization at any given temperature. These changes are indicative of changes in the viscosity and molecular weight (Hamm, 1983). Kyenge (2006) also reported similar results, though higher values were obtained. From Figure 6, it was established that refractive index increases with temperature of reaction; this increase being more pronounced for sulphur catalyst (Kyenge, 2006). Similar trends were obtained from the dimerization of MSO by Egbo (2006) and Uwakwe (2006) using iodine and NaHSO<sub>4</sub> catalyst systems respectively. However, the former obtained higher values of refractive index than the later. This shows that iodine catalyst is more suitable for the dimerization of melon seed oil than NaHSO<sub>4</sub>.

## Acid values

Acid values (AV) of the dimerized oil obtained at 5 min interval are plotted as functions of time and temperature and are shown in Figures 7 and 8 respectively. From these plots, it is evident that acid value increased steadily with time and temperature of the reaction. This is an indication that more acid groups were formed with increase in time and temperature. The observed increase could be due to the production of free fatty acids during the isomerization of bonds (Adams and Powers, 1946). It could also be traceable to the decomposition products formed as a result of higher temperatures employed (Anderson and Peter, 1949).

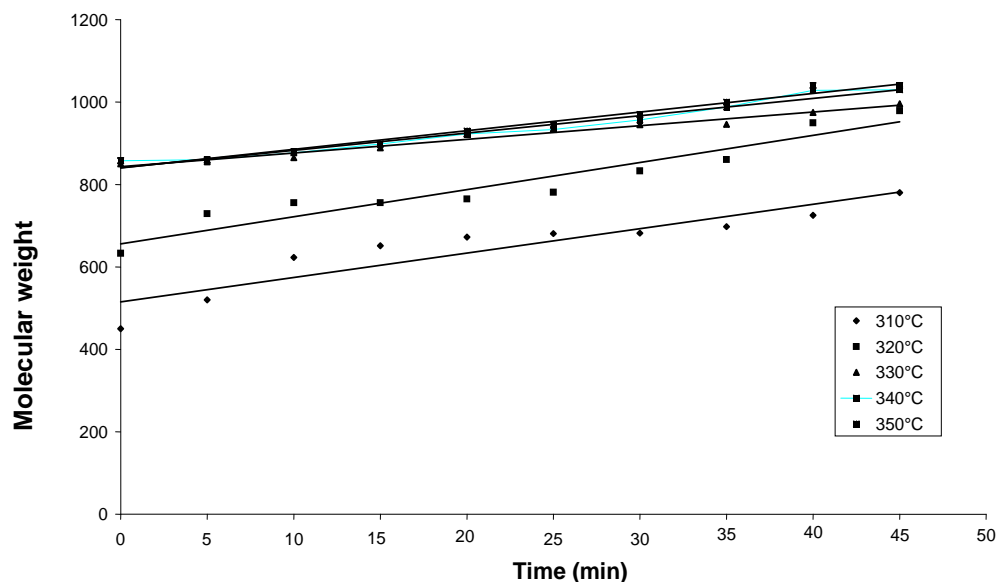


Figure 1. Plot of molecular weight versus time taken to dimerized PSO.

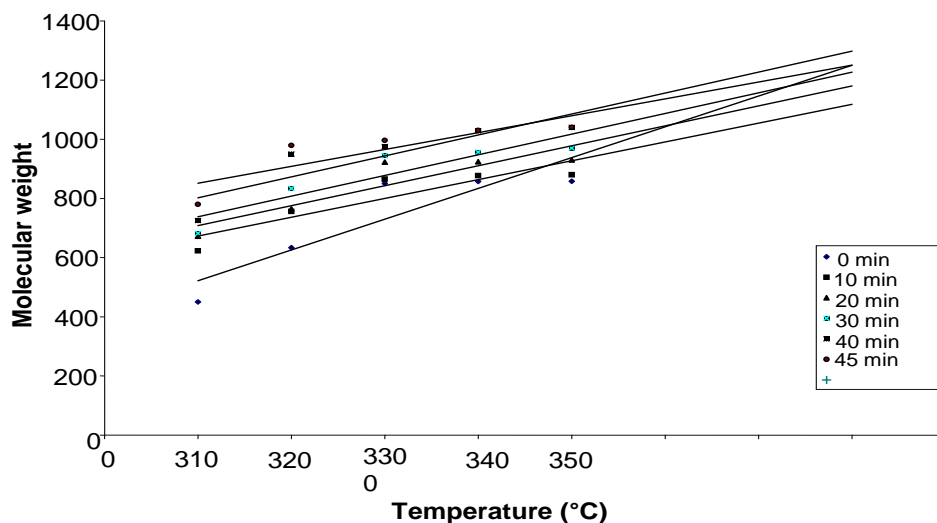


Figure 2. Plot of molecular weight versus change in temperature of the dimerized PSO.

However, at lower temperatures (310 to 320°C) the increase in acid values with time was not pronounced, probably due to the vaporization of most of the free fatty acids originally present. There was a substantial increase in the acid values at 330 to 350°C indicating that more thermally resistant free fatty acids might have been formed.

In this work, an acid value of 32.0 mg KOH/g was obtained at the optimum dimerization conditions of 350°C and 40 min. A comparable acid value of 33.6 mg KOH/g at the optimum dimerization conditions (350°C, 40 min) was obtained by Kyenge (2006) with sulphur catalyst, although slightly higher. Similar trends were also

obtained by Egbo (2006) and Uwakwe (2006) from dimerization of melon seed oil using iodine and NaHSO<sub>4</sub> catalyst systems respectively. Higher values were however obtained by Kyenge, showing that there was a higher level of chemical reactivity with iodine catalyst than NaHSO<sub>4</sub>.

#### Thermodynamic study: Enthalpy of dimerization

The enthalpy of dimerization of fatty acids,  $\Delta H_{DIM}$  could be estimated by measuring the property of the dimerized material that varies with temperature such as acid value

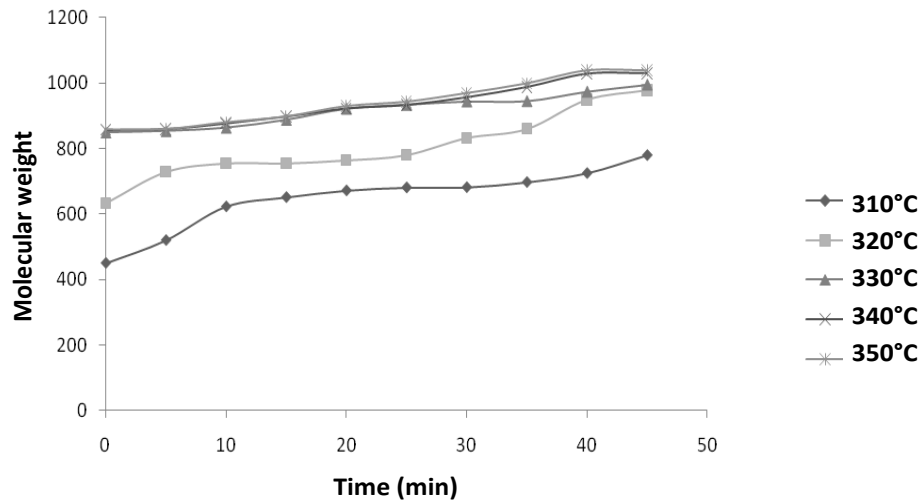


Figure 3. Plots of molecular weight versus time taken to dimerized PSO.

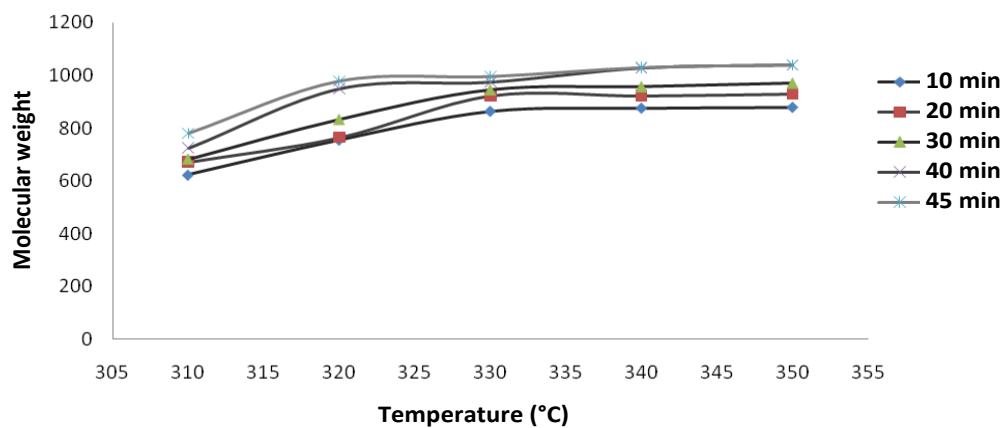


Figure 4. Plots of molecular weight versus time taken to dimerized PSO.

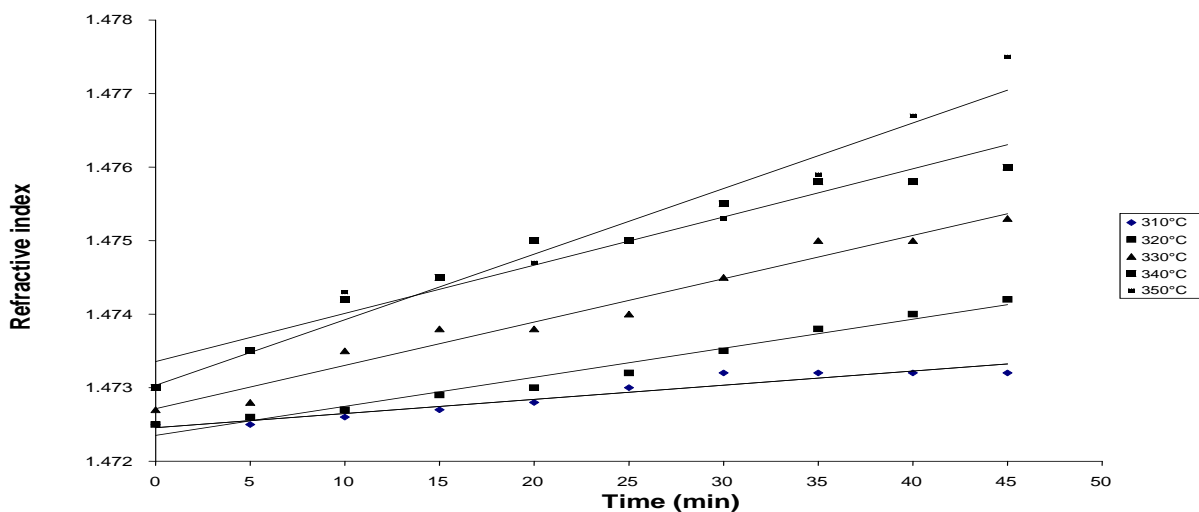


Figure 5. Plot of refractive index versus time taken to dimerized PSO.

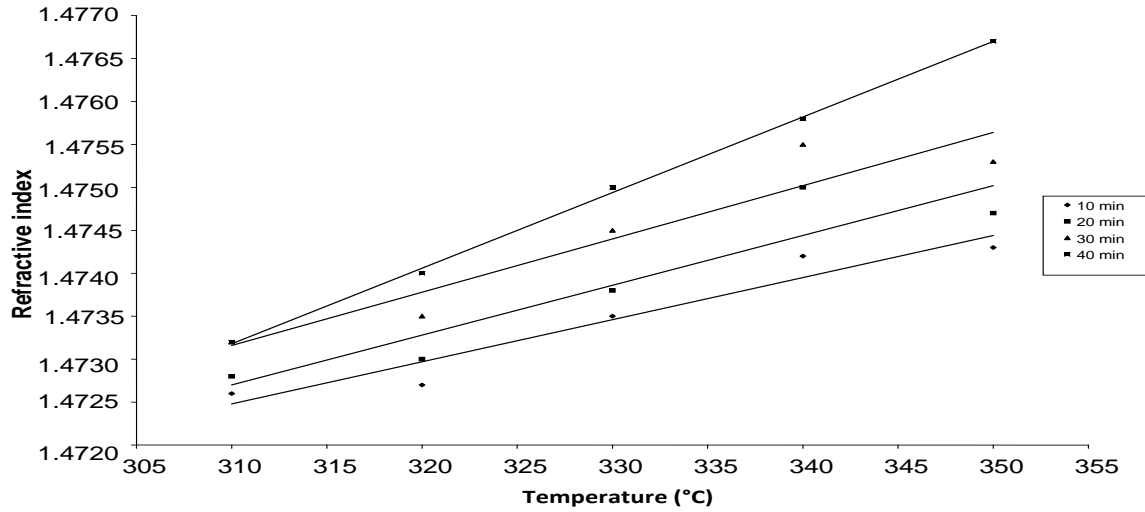


Figure 6. Plot of refractive index versus change in temperature of the dimerized PSO samples.

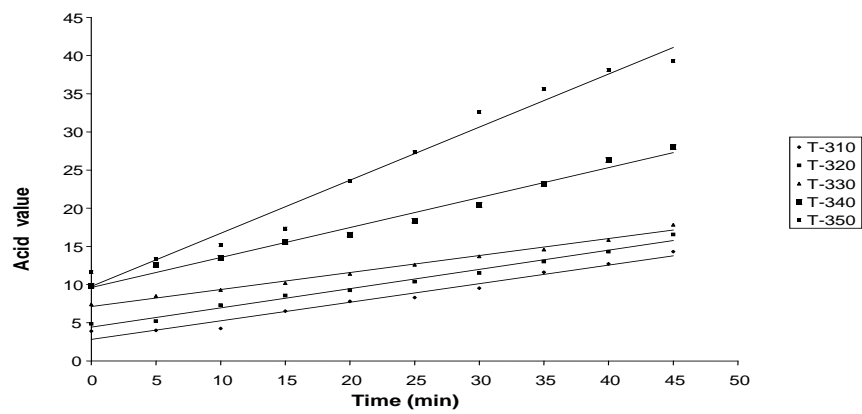


Figure 7. Plots of acid values versus time taken to dimerized PSO.

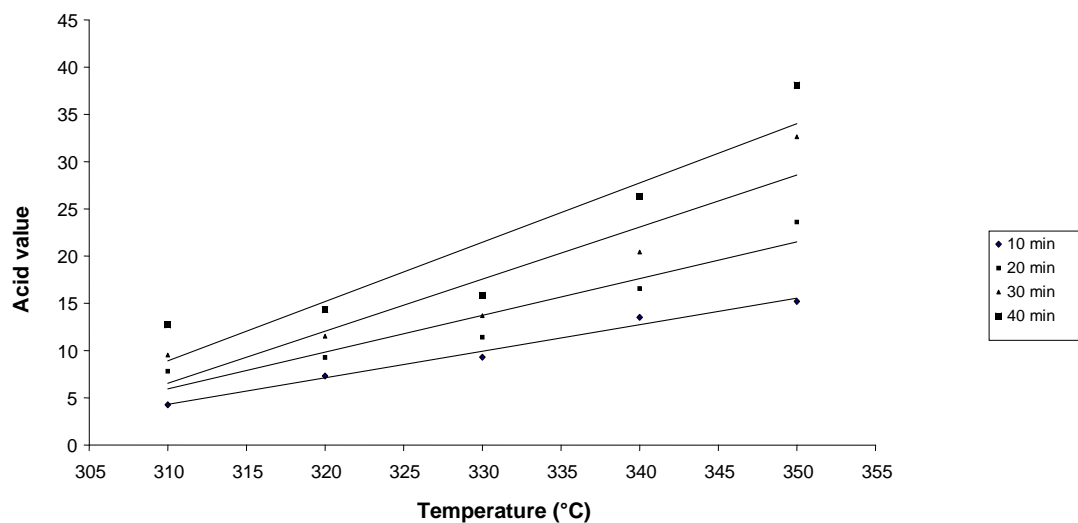
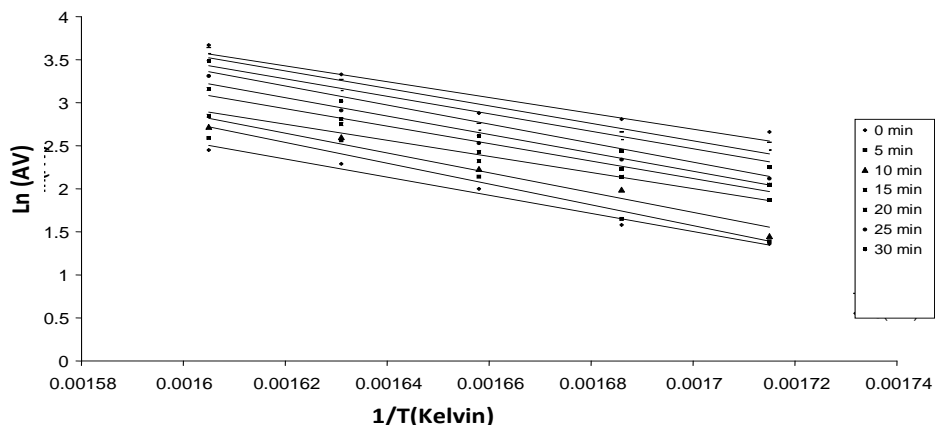


Figure 8. Plots of acid values versus change in temperature of dimerized PSO.



**Figure 9.** Plots of  $\ln(AV)$  versus  $1/T$  for dimerized PSO.

**Table 1.** Values of enthalpy change for different dimerization times.

Dimerization time (min)	Equation of the graph	$\Delta H_{DIM}$ (kJ)
0	$y = -10521x + 19.38$	-87.47
5	$y = -12081x + 12.109$	-100.44
10	$y = -14496x + 21.27$	-120.52
15	$y = -9347x + 17.893$	-77.71
20	$y = -10143x + 19.363$	-84.33
25	$y = -10686x + 20.37$	-88.84
30	$y = -11071x + 21.13$	-92.04
35	$y = -10149x + 19.72$	-84.38
40	$y = -10153x + 19.818$	-84.41
45	$y = -9181.9x + 18.303$	-76.34

**Table 2.** Comparison of enthalpy changes in dimerization of pumpkin seed oil.

Time (min)	$\Delta H$ (kJ)	
	Iodine	Sulphur*
0	-87.47	-62.484
10	-120.52	-60.258
20	-84.33	-57.073
30	-92.04	-57.921
40	-84.41	-53.531

\*Source: Kyenge (2006).

(Ejikeme and Ibemesi, 2007). Thus, the AV data were applied in the expression:

$$\ln(AV) = -\Delta H/RT + C$$

Plots of  $\ln(AV)$  versus  $1/T$  in (Kelvin) are shown in Figure 9. From the slopes of these plots, values of  $\Delta H_{DIM}$  for the reaction were obtained for different reaction times as

given in Table 1. The enthalpy changes obtained were compared with those of Kyenge as shown in Table 2.

Table 2 shows that iodine catalyst gave higher enthalpy changes than sulphur catalyst. This confirms that it is more exothermic and therefore more energetically favoured. However, the higher enthalpy changes did not give rise to higher molecular weights, refractive indices and acid values of the dimerized oil samples as earlier

**Table 3.** Results of TLC analysis.

Temperature (°C)	Average molecular weight of sample	% by weight of sample	Acid value	Fraction
330	580	71.58	16.83	Monomer
	960	4.8	5.61	Dimer
340	600	60.36	28.05	Monomer
	1000	18.58	22.0	Dimer
350	650	64.6	29.05	Monomer
	1080	18.7	39.29	Dimer

shown. The complexity of the dimerisation process in which a host of other reactions are involved, might account for this enthalpic order.

### Thin layer chromatography (TLC) analysis

TLC was carried out on selected samples of PSO dimerized at optimum time of 40 min (Malkar et al., 2000). This was followed by the cryoscopic determination of the molecular weights of the TLC fractions (Ibemesi, 2004). The results for the optimal reaction temperature are given in Table 3. For each of the temperature values, preparative TLC gave two (2) bands, which on elution with diethyl ether, gave two average molecular weights corresponding to monomer and dimer fractions respectively.

Within the limits of experimental error, the optimum yield of dimer fraction obtained through the iodine catalyzed dimerization of PSO was 18.7%, at a temperature of 350°C and reaction time of 40 min. This value when compared with the one obtained by Kyenge (42.5%) using sulphur shows that, sulphur is a better dimerization catalyst than iodine.

### Conclusion

At 350°C and 40 min of reaction, 18.7% of dimer product was obtained in the dimerization of PSO. The process was clearly exothermic. Molecular weight and acid value were observed to increase with temperature as well as time. There were also marked increases in the refractive index with time and temperature. On the whole, iodine appears less effective than sulphur in the dimerisation of PSO.

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