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Measurement and correlation of solubility of carbon dioxide in triglycerides

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ABSTRACT

A new pressure drop solubility gas apparatus was developed to determine the solubility of carbon dioxide in canola oil, a triglyceride consisting primarily of oleic, linoleic, and alpha linoleic acid radicals. Solubility of CO_2 in triglycerides was determined at different temperatures (283.2–303.2 K) and pressures (600–2450 kPa). It was found that the solubility of CO_2 in triglycerides is higher than that of pure water because triglycerides lack strong hydrogen bond networks that exist in liquid water at the ambient conditions. The experimental solubility was correlated using Krichevsky–Kasarnovsky (KK), Mather-Jou (MJ), and Carvalho-Coutinho (CC) correlations. We find that KK and MJ equations can predict the solubility with higher accuracy. The enthalpy and entropy of absorption of CO_2 were calculated using the van't Hoff plot and were found to be -7.165 kJ.mol^{-1}, and -28.791 J.mol^{-1}.K^{-1}, respectively.

1. Introduction

In the recent years, there has been intense research focused on developing efficient and cost effective technologies for transportation biofuels for securing energy, reducing environmental concerns and lessening foreign oil dependency [1–3]. One of the key components in a renewable energy portfolio is biodiesel, which is biodegradable, less toxic and has energy density similar to conventional petroleum diesel [4–6]. Oleaginous microorganisms are considered as one of the possible alternative feedstocks for biodiesel as they can accumulate more than 20% lipid on a dry weight basis [7]. To use these lipids as biodiesel feedstock, they must be first extracted from the microorganisms. The traditional Bligh and Dyer [8] method used to extract the lipid from the oleaginous yeast in the laboratory setting would be uneconomical on a commercial scale because of high extraction cost. The conventional oil extraction method [9] for oleaginous algae requires lipid source to be nearly free of water with solid content more than 90%. Since biomass drying accounts for more than 75% total energy consumption, the process becomes economically unfeasible [10]. However, the lipid recovery can be increased if the cell is disrupted prior to extraction, potentially decreasing the need to dry to ($\geqslant$90%) solids [11], and thus reducing the energy requirement for the process [12]. Efficient and economical cell lysing results in enhanced lipid extraction due to the increased mass transfer rates [13].

Some of the commonly available methods for microbial cell disruption are mechanical, physical, chemical, and enzymatic cell disruptions [14]. Cell lysing using chemical solvent is a useful technique that is able to disrupt the microbial cell wall by reacting with lipophilic tail, but seems to be unfeasible due to the cost of solvent recovery. Different solvents were tested to evaluate the feasibility of cell inactivation, and it was found that carbon dioxide is superior to other chemicals such as nitrogen, argon, tetrafluoroethane, etc. [15]. Lin et al. reviewed the microbial cell disruption using supercritical and subcritical CO_2 [16]. The lipid extraction cost using supercritical CO_2 (pressure and temperature above 7380 kPa and 304.5 K) is significantly higher; thus, a process utilizing subcritical CO_2 can potentially reduce the extraction cost. If the cell is disrupted using pressurized CO_2 prior to lipid extraction, the extraction kinetics enhances due to the reduced mass transfer limitation since carbon dioxide can penetrate through the phospholipid membrane of the cell [15]. CO_2 facilitates the disruption due to the high solubility of carbon dioxide in lipid. Furthermore, CO_2 is cheap, nontoxic, nonflammable, and naturally abundant [17].

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A thorough understanding of solubility of carbon dioxide in triglycerides is essential for designing efficient cell disruption processes. Although there is a large number of studies [18–22] conducted on solubility of triglycerides in super critical carbon dioxide for oil extraction, there is a lack of data on low pressure CO_2 solubility in triglycerides.

This paper presents an experimental design based on pressure drop gas apparatus that not only allows for the measurement of gas solubility but also cell disruption by applying pressure and vacuum in a cyclic manner. The solubility of CO_2 in canola oil, a triglyceride consisting primarily of oleic, linoleic, and alpha linoleic acid was measured at different temperatures and pressures. We selected canola oil because its fatty acid profile is very similar to the triglycerides produced by the microbes [7]. The experimental solubility was correlated with three thermodynamic models. Thermodynamic properties such as enthalpy of dissolution, entropy of dissolution and Gibbs energy of dissolution were determined using van't Hoff's plot.

2. Experimental

2.1. Materials

Refined canola oil was purchased from Fisher Scientific, USA. The iodine value, saponification value, acid value, and peroxide value of canola oil were 111, 190.3, 0.01, and 1.67 as described by the supplier. For the characterization of canola oil, its fatty acid compositions were determined, and compared with the available literature [23]. For fatty acid methyl ester (FAME) analysis, the refined canola oil was transesterified, and analyzed using Agilent 6890N gas chromatograph equipped with a flame-ionization detector (GC-FID; Agilent Technologies Inc., Wilmington, Delaware, USA) with a Zebron ZBFFAP column of 30 m with 0.25 mm inner diameter and film thickness of 0.25 μm, respectively. Each sample was injected three times in the GC. Helium was used as the carrier gas with a rate of 20 $mm^3.s^{-1}$ and the detector temperature was 533.2 K. Temperature was increased from 323 to 523 K with a rate of 16.67×10^{-2} K s^{-1} [24]. The instrument was calibrated using a standard solution containing known concentration of C9–C24 FAMEs (Sigma Aldrich, USA) [24]. The results of fatty acid obtained from GC analysis are shown in Table 1 along with literature values. Most common fatty acids found in the canola oil were oleic acid (C18:1), linoleic acid (C18:2), linolenic acid (C18:3), and palmitic acid (C16:0) (Supplementary Material, Fig. S1). The fatty acid compositions of canola oil were found to be nearly identical to the available literature [23]. The fatty acid compositions of canola oil were also compared with OM, and found to be similar for oleaginous yeast [7]. The molecular weight of canola oil was determined from its fatty acid composition. The procedure for finding the molecular weight from the fatty acid profile can be found in the literature [25]. The obtained molecular weight of canola oil is provided in Table 2, which was found to be the same as reported by Leung et al. and Singh et al. [26,27]. A little deviation from the previous work was found due to the variation in fatty acid profile of the present canola oil sample. The water content in the canola oil was determined using volumetric Karl-Fischer titration by the authors and reported as g water/g canola oil, which is provided in Table 2. Carbon dioxide was purchased from Nexair, Columbus, Mississippi. The deionized water from the laboratory was used to determine the solubility of CO_2 in water. Table 2 provides the summary of chemicals used for this research along with their purity, source, and purification method. The purity of both CO_2 and tetradecane was provided by the supplier and used for the experiment without further purification.

2.2. Apparatus and experimental procedure

The experimental set-up is shown in Fig. 1. A dual reactor system was used for measuring the solubility of CO_2 in liquids. Two pressure vessels of capacity of 650 and 450 mL, respectively, were purchased from Parr Instrument, USA. Pressure vessel 1 was used for measuring the amount of gas injected initially in the system, and pressure vessel 2 was used for measuring the solubility where a known amount of solvent was placed initially. Pressure vessel 2 was equipped with a stirrer to maximize the contact between the gas and the liquid; hence, equilibrium was obtained in a reasonable time. A type J thermocouple (T) with an uncertainty of ±0.1 K inserted into pressure vessel 2 was used to measure the temperature in the system. A Neslab RTE10 recirculating water bath chiller purchased from Thermo Scientific, USA was used to maintain a uniform temperature in both vessels. Ethylene glycol was the circulating fluid in the chiller that maintains the uniformity of temperature in both vessels. A single-phase high vacuum pump, purchased from Edwards, was used for degassing the solvent. A pressure transducer purchased from Ashcroft, was used to measure the pressure in the system. The accuracy of the pressure transducer is 0.05% with the minimum and maximum reading of 0 and 13,789 kPa, respectively. The resolution of the pressure transducer is 0.1 psi. Before each run, the degassing was conducted three times (each at least 20 min) for the complete removal of any impurities present in the solvent. For degassing, valves V_3 and V_4 were kept open and all other valves remain closed. After degassing, valves V_3 and V_4 were closed, and CO_2 was injected into pressure vessel 1 by opening valves V_2 and V_5. When the pressure was stabilized in vessel 1, the initial gauge pressure from the pressure transducer, atmospheric pressure from the barometer, and the temperature from the thermometer were recorded and the amount of total gas charged into vessel 1 and the tubing was determined.

After pressure stabilization in vessel 1, valve V_6 was opened and the gas came into contact with the liquid present in vessel 2. A constant stirring was applied in vessel 2 throughout the experiment for gas-liquid mixing. After reaching the equilibrium (when there

Table 1
Comparison of fatty acid composition of refined canola oil with literature [23].[a]

Fatty acid[d]	M[b]/(g/mol)	$C_{x:y}$[c]	100 w (This Work)	100 w (Literature)
Palmitic	256.42	$C_{16:0}$	4.77 ± 0.05	3.6
Palmitoleic	254.41	$C_{16:1}$	0.40 ± 0.01	0.2
Stearic	284.47	$C_{18:0}$	1.73 ± 0.03	1.5
Oleic	282.46	$C_{18:1}$	63.03 ± 0.40	61.6
Linoleic	280.44	$C_{18:2}$	21.45 ± 0.20	21.7
Linolenic	278.43	$C_{18:3}$	7.57 ± 0.07	9.6
Arachidic	304.46	$C_{20:4}$	0.80 ± 0.20	–

[a] Experimental results for fatty acid composition is reported together with its standard uncertainty.
[b] Molar mass.
[c] $C_{x:y}$; x: number of carbons, y: number of double bonds.
[d] Behemic and Erucic acids are present in trace amounts.