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AUGMENTING FRYING STABILITY OF SOYBEAN OIL BY INCORPORATION OF CURCUMIN

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ABSTRACT

Turmeric (*Curcuma longa*) belongs to the family Zingiberaceae and is also known as the golden spice. Curcumin is an important component isolated from turmeric that is used as a traditional medicine as well as an additive (antioxidant) in food products. The study was aimed at analyzing the effect of curcumin addition on soybean oil after repeated frying cycles. This study was an experimental study which comprised of two turmeric samples (Sample-RW and Sample-MS) which were subjected to various physico-chemical tests as per FSSAI. Curcumin was extracted from both the turmeric samples using Soxhlet apparatus (95% ethyl alcohol). The highest curcumin extracted was further incorporated in soybean oil @0.1g-0.5g/100ml. The soybean oil containing different concentrations of curcumin were subjected to repeat frying and chemical analysis was further performed and correlated.

Keywords: *Curcumin, antioxidant, soybean oil, frying, etc.*

I. INTRODUCTION

Turmeric (Curcuma *longa*) belongs to the family Zingiberaceae and is also known as the golden spice (Jyothi et al, 2003). India is the largest producer, consumer and exporter of turmeric in the world (Anandaraj et al, 2014). The yellow orange coloration of turmeric powder is due to the presence of curcuminoids present in them (Siviero et al, 2015). The curcuminoids are a mixture of curcumin, mixed with its two derivatives demethoxy-curcumin (DMC) and bis-demethoxy-curcumin (BDMC) (Joshi et al, 2009). Curcumin is highly stable in acidic solutions and hence remains stable throughout the process of digestion. According to a joint Food and Agriculture Organization/ World Health Organization (FAO/WHO) report on food additives, the recommended maximum daily intake of curcumin is 0-1mg/Kg body weight(Sharma et al, 2004; Cheng et al, 2001).

Frying is a common and popular cooking method, which gives food its palatability, because of fat absorption, crust formation and desired flavor (Maskan et al, 2015). The major concern in frying oils is the lipid oxidation (Kathirvel and Rupansinghe, 2011). The most preferable way to inhibit the lipid oxidation mechanism is by the use of antioxidants (Maskan et al, 2015). Curcumin has shown to inhibit lipid oxidation by 82% (Priyadarsini et al, 2003). In vitro studies, curcumin has shown to be at least 10 times more active as an antioxidant than alpha-tocopherol (Khopde et al, 2000). Curcumin can be used as powerful antioxidant and can be added in small amounts to the frying oils to prevent rancidity.

The aim of the study was to make frying oil thermally stable with the use of natural antioxidant like curcumin from turmeric. Curcumin being a natural source is preferred than synthetic antioxidants. Since the use of curcumin as a potent antioxidant has not been explored much as yet, therefore the present study aims to prove its potency as an effective antioxidant for oils.

Curcumin

Curcumin, a polyphenol found in turmeric is present at a concentration of 3%-5% (Shimatsu et al, 2012). Curcumin is a symmetric molecule, also known as diferuloyl methane. The International Union of Pure and Applied Chemistry (IUPAC) name of curcumin is (1E, 6E)-1, 7-bis (4-hydroxy-3-methoxyphenyl)-1, 6-heptadiene-3, 5-

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dione, with chemical formula $C_{21}H_{20}O_6$. And has a molecular weight of 368.38 (Priyadarsini, 2014). Curcumin is almost insoluble in water and readily soluble in polar solvents like methanol, ethanol, acetonitrile, chloroform, ethyl acetate, etc. It is sparingly soluble in hydrocarbon solvents like cyclohexane and hexane. Curcumin is recognized as safe food in the US (Shimatsu et al, 2012). The absorption spectrum of curcumin has two strong absorption bands, one in the visible region with maximum ranging from 410-430 nm and another band in the ultraviolet (UV) region with maximum at 265 nm region (Priyadarsini, 2014).

Curcumin as an Antioxidant

Lipid peroxidation is a major cause of oil degradation. It is a common problem among edible oils and results in sensory changes known as oxidative rancidity. It is one of the major reasons for oil rejection among consumer. Rancidity causes undesirable chemical change in flavor, color, odor and nutritional value. Furthermore, it also promotes formation of free radicals such as hydroxyl and peroxyl radicals, which are associated with mutagenesis, carcinogenesis and ageing (Ramadan, 2013).

The conventional method of preserving or reducing the rate of rancidity is by adding tocotrienol or α-tocopherol. The addition of vitamin E derivatives carries a risk of exceeding their optimal concentration of 400-800 mg/day, which may cause it to exhibit pro-oxidant properties (Esterbauer et al, 1991). Plant extract exhibit a high level of antioxidant activity due to their phytochemical content. Phytochemical may be as much as 50 times more potent than vitamin E and 20 times more potent than vitamin C (Ling et al, 2009 and Palanisamy et al, 2008). Curcumin has shown to exert an antioxidant effect by removing free radicals and an anti-inflammatory effect by inhibiting the activation of Nuclear Factor Kappa-light-chain-enhancer of activated B cells (NF-Kb) (Aggarwal et al, 2007). Curcumin has been more effective in preventing lipid peroxide formation than the synthetic antioxidant BHT. The principal coloring components of curcumin scavenge free radicals at the cost of becoming weak free radicals. According to one research report these second hand free radicals are unreactive and short-lived products (unlike those of synthetic phenolics, e.g.BHT or BHA) and do not pose a health hazard (Majeed et al, 2000).

Curcumin has been found to be an excellent scavenger of most radicals, a property that bestows curcumin with antioxidant activity in normal cells (Priyadarsini, 2009; Mishra et al, 2004; Jovanovic et al, 2001). Curcumin undergoes much faster degradation when exposed to sunlight. The colorless products identified during photo degradation of curcumin are vanillin, ferrullic acid and other small phenols (Priyadarsini, 2014).

In general it has been observed that complexation with curcumin reduces the toxicity of the metals and some curcumin complexes with metals like copper ion (Cu^{2+}), manganese ion (Mn^{2+})' and act as new metal based antioxidants. Due to the reversible electron transfer reactions with superoxide ions, $Cu^{2+}$and Mn^{2+} complexes of curcumin act as superoxide dismutase enzyme mimics.

Fats and Oils: Rancidity and its prevention

Fat is an important component of diet. It is a concentrated source of energy, imparts palatability to the diet and retards stomach emptying time (Gopalan et al, 2004). It also enhances texture, taste and flavor of food and reduces bulk in the diet. Further it is an excellent source of fat-soluble vitamins A, D, E and K. It plays a part in the biosynthesis of several long chain fatty acids and provides essential fatty acids, which are components of membranes of living cells (Srilakshmi, 2007).

Fats and oils are chemically known as triacylglycerols (TAG). Triacylglycerols or triglycerides as they are often called are triesters of glycerol and fatty acids. Triglycerides usually contain two or three different fatty acids and are known as mixed triglycerides. Therefore, fats and oils are mixtures of different mixed triglycerides and contain a number of different fatty acids.

Soybean Oil

Soybean is the dominant oilseed produced in the world, due to its favorable agronomics characteristics, its high quality protein and its valuable edible oil. Soybean oil contains various classes of lipids. But primarily it consists of neutral lipids, which include tri-, di- and monoglycerols, free fatty acids and polar lipids such as phospholipids (Gunstone, 2002).

Frying

Deep fat frying is commonly used worldwide for the preparation and manufacture of various foods. Frying is a process that involves immersing food in hot oil with contact of oil, air and food at high temperature. It is a unit operation, which is mainly used to alter the eating quality of food (Fellows, 2000). Frying oil acts as a heat transfer medium and contributes to the texture and flavor of the fried food (Romano et al, 2012). The oil used for frying must have good flavor and oxidative stability in order to achieve good shelf life for the fried products (Gulla et al, 2012). During frying it is observed that there is loss of essential Polyunsaturated Fatty Acid (PUFA) (Farhoosh et al, 2009). Studies have shown that oils having a higher content of PUFA were more susceptible to oxidation (Kapich et al, 2010).

II. METHOD & MATERIAL

Procurement of Raw Materials: The raw materials were procured from the local market of East Delhi, India. The standard curcumin was purchased from Merck and the soybean oil samples (with and without addition of antioxidants) were procured from Goyal Mill, Delhi.

Physico-chemical Analysis of Turmeric Samples: Both the turmeric samples RW (dried rhizome powder) & MS (procured from market) were subjected to physico-chemical analysis. The tests included moisture analysis (Oven Drying Method: AOAC, 2000), ash content (Gravimetric Method: I.S 1797-1985), acid insoluble ash (I.S 1797-1985) and lead chromate test (I.S 3576-1994).

Extraction and Estimation of Curcumin from Turmeric Samples: Curcumin extraction was carried out through soxhlet apparatus using ethyl alcohol (95%) as solvent (IS: 3576-1994). The process was carried out for 6 hours. And the estimation of curcumin was carried out using Spectrophotometric analysis, using Standard curcumin (Merck) as standard.

Extraction of Curcumin for Incorporation into Soybean Oil: About 5g of turmeric powder (which yielded the highest curcumin concentration) was taken in a thimble, and put in an extractor closed with a cotton plug. The solvent i.e. ethyl alcohol (95%) was taken in a distillation flask. The apparatus was set on a heating mantle and allowed to reflux for 6 hours. The extracts were further kept in airtight amber colored bottles. The solvent was evaporated using Rotary Vacuum Evaporator at 68.7˚C separately, and was then dried in oven at 100˚C for 5 hours (Verma, 2014).

Incorporation of Curcumin in Soybean Oil Samples: The dried curcumin extract was incorporated into soybean oil (without any antioxidant) samples at concentrations from 0.1g to 0.5 g/100ml and stirred continuously on a magnetic stirrer until mixed. Afterwards, puffs were fried (made up from wheat flour, corn flour and rice flour) at 180˚C for 1minute and thereby oil was heated continuously for 8 hours for three consecutive days (240 hours). The oil after heating was cooled at room temperature and stored under refrigerated conditions for the consecutive use on the next day. It was made sure that no oil was replenished the next day before the frying process. The oil (with artificial antioxidant TBHQ) was also subjected to the same process for three days.

The oil samples were further tested for Free Fatty Acid (940.28: AOAC, 1995), Peroxide value (965.33 (AOAC, 1995), and Acid Value (ISI Handbook of Food Analysis, 1996) on each day post frying operation for three days, before keeping in the refrigerated condition.

III. RESULTS & DISCUSSION

Physico-chemical Analysis of Turmeric Samples: The physico-chemical test results are depicted in Table 1. All the parameters were within the reference range as per ideal standards. Moisture level above 12% can affect the freeflow characteristics of turmeric powder. The moisture content of sample-RW and sample-MS were found to be within the range. The higher moisture content of sample-RW could be due to inappropriate drying and storage conditions of the dried rhizomes.

Ash is incombustible residue of any substance i.e. the remains of a completely burnt material, the dust is powdery substance to which a material is reduced after complete combustion. Chemically ash consists of non-volatile inorganic constituents of the burnt substance. The major constituents of ash of spices in particular are calcium (Ca), phosphorus (P), iron (Fe), sodium (Na), potassium (K), halogens, silica and sand or siliceous matter. Combustion evaporates moisture and oxidizes organic matter to vanish in air. According to FSSA (2006) the reference range for ash content is not more than 9% by wt. for ground turmeric. Therefore, the ash content of the turmeric samples was found within the standard range. However, the ash content of sample-RW was found to be higher as compared to sample-MS indicating that sample-RW had higher inorganic matter than sample-MS. The ash content of spices is also a determinant for quality and lower ash content means that sample-MS was more refined or made of good quality rhizomes. The Acid-Insoluble Ash Test is designed to measure the amount of ash insoluble to diluted hydrochloric acid. The acid insoluble ash is then determined, from the mass of the insoluble residue after ignition and the dry matter content of the sample. The acid insoluble ash content of both the turmeric samples was found to be within range. Lead chromate is used to polish the extracted whole turmeric to give a genuine appearance (Sathe, 1999). Hence it is considered an adulterant for turmeric. Both the samples tested negative for lead chromate. This indicated that both the samples were not adulterated and hence were fit to consume.

Table 1: Physico-chemical Test Results for Turmeric Powder

Parameter	Sample-RW	Sample-MS	Reference
Moisture content (%)	8	6	Not more than 10% by wt.
Ash Content (%)	6.45	6.91	Not more than 9% by wt.
Acid Insoluble Ash (%)	0.5	1.05	Not more than 1.5% by wt.

* Values are represented as Mean±SD of triplicate readings. Sample-RW: Dried rhizome powder; Sample-MS: Market sample of turmeric powder

Estimation of Curcumin Content: The curcumin (%) of sample- RW and MS was analyzed to be 13.26% and 16.09% respectively. The yield of extracted curcumin was found to be slightly higher than the amount mentioned in a study conducted by Soni et al (2011) which was 10.23%.

Physico-chemical Analysis of Oil Samples: All the oil samples were subjected to tests such as peroxide value, free fatty acid and acid value. The various tests results are depicted in Table 2, Table 3, and Table 4 respectively.

Table 2: Test Results of Peroxide Value for Soybean Oil Samples

Peroxide Value (Meq)	Sample-C	Sample-V_1	Sample-V_2	Sample-V_3	Sample-V_4	Sample-V_5	Sample-MS
Day 1	1.4±0.05	1.4±0.13	1.2±0.45	1.07±0.001	1±0.21	0.98±0.11	0.8±0.06
Day 2	1.8±0.14	1±0.90	0.99±0.01	0.98±0.005	0.78±0.22	0.80±0.26	1.1±0.09
Day 3	3.6±0.12	0.6±0.24	0.6±0.04	0.59±0.43	0.58±0.001	0.2±0.05	1.4±0.04

* Values are represented as Mean±SD of triplicate readings. Sample-C: control i.e. soybean oil without any added antioxidant; Sample V_1- V_5: Variation of soybean oil with added curcumin @0.1-0.5g/100ml respectively & Sample-MS: Market soybean oil sample containing artificial antioxidant

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Table 3: Test Results of Free Fatty Acid for Soybean Oil Samples

Free Fatty Acid (%)	Sample-C	Sample-V_1	Sample-V_2	Sample-V_3	Sample-V_4	Sample-V_5	Sample-MS
Day 1	0.3±0.34	0.22±0.05	0.21±0.005	0.22±0.01	0.20±0.12	0.22±0.33	0.25±0.90
Day 2	0.36±0.01	0.22±0.67	0.20±0.34	0.20±0.76	0.17±0.55	0.17±0.008	0.3±0.21
Day 3	0.45±0.45	0.21±0.005	0.20±0.009	0.20±0.11	0.15±0.06	0.14±0.65	0.32±0.04

* Values are represented as Mean±SD of triplicate readings. Sample-C: control i.e. soybean oil without any added antioxidant; Sample V_1- V_5: Variation of soybean oil with added curcumin @0.1-0.5g/100ml respectively & Sample-MS: Market soybean oil sample containing artificial antioxidant

Table 4: Test Results of Acid Value for Soybean Oil Samples

Acid Value	Sample-C	Sample-V_1	Sample-V_2	Sample-V_3	Sample-V_4	Sample-V_5	Sample-MS
Day 1	0.42±0.34	0.31±0.05	0.30±0.005	0.31±0.01	0.30±0.12	0.31±0.33	0.35±0.90
Day 2	0.51±0.01	0.31±0.67	0.30±0.34	0.30±0.76	0.24±0.55	0.24±0.008	0.42±0.21
Day 3	0.64±0.45	0.30±0.005	0.30±0.009	0.30±0.11	0.21±0.06	0.20±0.65	0.45±0.04

* Values are represented as Mean±SD of triplicate readings. Sample-C: control i.e. soybean oil without any added antioxidant; Sample V_1- V_5: Variation of soybean oil with added curcumin @0.1-0.5g/100ml respectively & Sample-MS: Market soybean oil sample containing artificial antioxidant

Correlation between Curcumin Concentration and Various Physico-chemical Parameters: A correlation was studied (as depicted in Table 5) using a statistical test between curcumin concentration and the various physic-chemical parameters of soybean oil (containing curcumin as an antioxidant).

Table 5: Correlation Coefficient for association between Curcumin Concentration & Physico-chemical Parameters

Peroxide Value (PV)	**Correlation Coefficient (r)**
Day 1	-0.95^{*}
Day 2	-0.87^{NS}
Day 3	-0.74^{NS}
Free Fatty Acid (FFA)	**Correlation Coefficient (r)**
Day 1	-0.18^{NS}
Day 2	-0.95^{*}
Day 3	-0.93^{*}
Acid Value (AV)	**Correlation Coefficient (r)**
Day 1	0^{NS}
Day 2	-0.90^{*}
Day 3	-0.88^{*}

* Correlation is significant at the 0.05 level of significance ($p<0.05$)
^{NS} Non- Significant

The relationship between curcumin concentration and the various tests for stability of oil like PV, FFA and AV were studied. It was observed that a negative correlation exists between curcumin concentration and the various parameters for oil stability. This indicated that as the curcumin concentration increased the parameters evaluated for stability of oil (i.e. PV, FFA and AV) decreased. Hence it can be concluded that curcumin may act on the oxidation products and help in retarding the oxidation process.

IV. CONCLUSION

India is the largest producer of turmeric in the world; still its usage is limited to its medicinal and therapeutic value. The curcuminoids present in turmeric can be a boon to the food industry, especially fats and oils (since they are more prone to oxidation) due to its antioxidative properties. The requirement for a natural antioxidant is the need of an hour. Since the synthetic antioxidants used in fats and oils may pose carcinogenicity, as well as are labile to frying temperatures and get easily volatilized. Hence the curcumin obtained after the extraction from turmeric, could easily be incorporated into oils. Since curcumin is oil soluble pigment and is not heat sensitive. Therefore its use as an antioxidant is explored in this study. Hence it can be concluded that curcumin may act on the oxidation products and help in retarding the oxidation process and can act as a potent antioxidant for fats and oils.

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