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CATALYTIC TRANSFER HYDROGENATION OF VEGETABLE OILS USING ULTRASOUND- A REVIEW

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Abstract: The utilization of Catalytic Transfer Hydrogenation (CTH) reaction using ultrasound for hydrogenation of vegetable oils has been investigated over a conventional hydrogenation process which is quite costly & hazardous. Conventional hydrogenation process of vegetable oils has significant fire hazard & potential risk factors due to use of highly flammable hydrogen gas, reagents & solvents. CTH process does not require such explosive gases, high pressure & temperature reactions as it is carried out at ambient conditions by using hydrogen donor such as ammonium formate (NH_4HCO_2), palladium supported on carbon (Pd/C) as the catalyst & water as a solvent. The ultrasonic cavitation approach is used to break carbon-carbon double bonds (C=C) of polysaturated fats & useful for conversion of vegetable oils into value added product. Also use of water as a solvent deals with a greener processing approach in the economical way with reduction in cost of high pressure hydrogenation process.

Index Terms - **Catalytic transfer hydrogenation, ultrasonic cavitation, hydrogen donor, vegetable oil**

I. INTRODUCTION

Vegetable oils are generally polysaturated fats with many carbon-carbon double bonds (C=C) within its structure. These fats are normally liquids at room temperature. We can hydrogenate or add hydrogen to these double bonds by passing hydrogen gas over the molecules in the presence of catalyst to convert polysaturates to monosaturates. When these fats are hydrogenated they get harden & results in higher melting points & becomes solids at room temperature. Most conventional vegetable oil hydrogenation process uses gaseous hydrogen at relatively high temperature & pressure in the presence of metal catalyst. Some reagents which are highly flammable and can ignite solvents and hydrogen especially dangerous after having been used for the hydrogenation. The use & presence of hydrogen gas increases the considerable risk of explosion. Catalytic Transfer Hydrogenation (CTH) using ultrasound is a promising alternative method for conventional hydrogenation process[1]. As we know that hydrogen gas is obtained from fossil fuels which can influence the environment unfavorably. The use of hydrogen donor instead of hydrogen gas along with suitable catalyst in CTH received a great deal of attention due to safety concerns, economy & sustainable features[2]. The method offered good selectivity ultrasonic approach also eliminates the operational difficulties such as high temperature control, poor conversion & use of high pressure reactors[3][4]. The byproducts which are obtained in this process are also biodegradable. Hydrogenation process improves the various physical & chemical properties of vegetable oils, since they are derived from natural sources & required some modifications in their structure & properties for better health benefits. The properties such as color, flavor, melting point, acid value, iodine vale, degree of unsaturation etc. may be changed in hydrogenated products[4]. CTH increases the rate of mass transfer along with higher selectivity of oil. The efficacy of CTH is based on applied catalyst with significant amount in order to ease of separation from product[5]. Also low energy consumption has been observed in the overall process of CTH.

To establish the importance of CTH, it is necessary to analyze the existing literature. Some major result outcomes are as follows:

SR NO.	AUTHOR	TITLE	RESULT OUTCOMES /FINDINGS
[1]	A. Smidovnik A. Stimac J. Kobe (1992)	Catalytic Transfer Hydrogenation of soybean oil	Various hydrogen donors & different solvents for CTH of soybean oil with Pd/C catalyst was investigated in batch as well as continuous process. The best results for final product were obtained with sodium formate donor along with water as a solvent at 60°C temperature.
[2]	A. A. Banerjee, D. Mukesh (1989)	Heterogeneous catalytic transfer hydrogenation reactions of 4-nitrodiphenylamine	Palladium (Pd) catalyst is found to be more active & suitable than Raney nickel for the transfer hydrogenation reaction.
[3]	Manoj A. Tike, Vijaykumar, V. Mahajani (2006)	Studies in catalytic transfer hydrogenation of soybean oil using ammonium formate as donor over 5% Pd/C catalyst	Ammonium formate solution (aqueous) with Pd catalyst was investigated for soybean oil CTH & observed good selectivity in final product.
[4]	Sonam V. Sancheti, Parag R. Gogate (2016)	Ultrasound assisted selective catalytic transfer hydrogenation of soybean oil using 5% Pd/C as catalyst under ambient conditions in water	Ultrasound assisted CTH process was observed at different temperatures. Excellent progress of hydrogenation has been reported at even 30^0C with ammonium formate as most effective hydrogen donor for soybean oil.
[5]	McArdle, S; Girish, S; Leahy, JJ; Curtin, T (2011)	Selective hydrogenation of sunflower oil over noble metal catalysts	As compared to platinum & nickel catalyst, palladium was found to be most suitable & effective catalyst & giving the best enhanced selectivity for hydrogenation of sunflower oil.
[6]	Dr. E. Fedeli, Dr. G. Jacini (1976)	Homogeneous Selective Catalytic Hydrogenation of Soybean Oil	For transfer hydrogenation of soybean oil use of homogeneous catalyst was studied.
[7]	Amikam Zoran, Yoel Sasson (1983)	Catalytic transfer hydrogenation of unsaturated compounds by solid sodium formate in the presence of palladium on carbon	Sodium formate in solid form as an efficient hydrogen donor has been reported for Pd/C-catalyzed transfer hydrogenation of olefins in the presence of an equimolar amount of water at exceedingly mild conditions.
[8]	Damin Zhang, Feiyang Ye, Teng Xue (2013)	Transfer hydrogenation of phenol on supported Pd catalysts using formic acid as an alternative hydrogen source	In transfer hydrogenation of phenol high activity of Pd/C catalyst was observed under mild conditions of bio-oil by converting unstable compounds to stable ones.
[9]	A. N. Sarve, M. N. Varma, S. S. Sonawane (2016)	Ultrasound assisted two-stage biodiesel synthesis from non-edible *Schleichera triguga* oil using heterogeneous catalyst: Kinetics and thermodynamic analysis	Ultrasound assisted heterogeneous catalytic system enhances biodiesel conversion shows higher reaction rates and ease of separation of glycerine & biodiesel with respect to reducing purification time and energy.

[10]	Ketaki D. Sarnaik, Parag R. Gogate (2019)	Intensified Catalytic Transfer Hydrogenation of Sunflower Oil Using Ultrasound	CTH of sunflower oil with ultrasound approach gave increased iodine reduction at lower temperature reaction & acid value reduction also.
[11]	P. N. Dange, A. V. Kulkarni, V. K. Rathod (2015)	Ultrasound assisted synthesis of methyl butyrate using heterogeneous catalyst	Various parameters was tested for synthesis of methyl butyrate with ultrasonic frequency & heterogeneous catalyst. It has been reported that the ultrasound assisted reaction gives best results.
[12]	Naglic, M.; Smidovnik, A.; Koloini, T. (1998)	Kinetics of Catalytic Transfer Hydrogenation of some vegetable oils	For CTH of various vegetable oils 10% Pd/C was reported the best suitable catalyst under various operating conditions.
[13]	Sonam V. Sancheti, Parag Gogate (2017)	A review of engineering aspects of intensification of chemical synthesis using ultrasound	Sonochemistry or ultrasound approach offers considerable potential for green and sustainable processing with efficient scale up procedures.

Table 1: Literature review of CTH of vegetable oil

II. SELECTION OF OIL

Hydrogenated vegetable oil is generally made from edible oils which are extracted from plants such as sunflower, soybean, olive, mustard etc. These oils are typically liquid at room temperature & required hydrogenation process to get more solid consistency. Hydrogen molecules are added in these liquid oils to alter the various parameters like texture, stability & its shelf life. It also improves the taste of product. After hydrogenation process these oils became more stable & resistant to oxidation which breaks fats when exposed to heat. That's why they are useful for fried & baked foods, as percentage of rancidity is less compare to other fats.

VEGETABLE OIL	UNSATURATED FATTY ACIDS (%)	IODINE VALUE
Sunflower	84.6	125-140
Soybean	79.3	138-143
Corn	80.5	103-128
Canola	88.5	91-126
Olive	78.1	75-94
Hazelnut	86.2	83-90

Table 2: Different vegetable oils with iodine value & unsaturated fatty acid percentage

The maximum percentage or degree of unsaturated fatty acids in oil, the more vulnerable it is to lipid peroxidation (rancidity). This unsaturation is in the form of carbon-carbon double bonds which react with iodine compounds & increase iodine value. Since in the hydrogenation process hydrogen atoms added to the oil & it will reduce the percentage of unsaturated fatty acids & increases the percentage of saturated fatty acids in the oil. The CTH process is useful for all these types of vegetable oil with greater percentage of unsaturated fatty acids & higher iodine value as shown in table 2.

III. EXPERIMENTAL SET UP

For CTH of oil an ultrasonic bath is required which is a dual frequency reactor with capability of operating at 22 & 40 kHz as a source of ultrasound [10][4]. The power dissipation is varied over 50 to 200 W range. Approximately 100 mL glass reactor with 50mm internal diameter & four baffles are required for the reaction. The reactor should be immersed in the bath at a constant distance of 2.5 cm from bottom with glass turbine inside. The complete experimental setup for ultrasonic assisted approach is shown in fig.1. Typically the CTH reactions was performed for 2 hours fixed reaction time with regular intervals & samples withdrawn for the analysis of iodine value (IV). Different experiments were performed to check the effect of amount of solvent, hydrogen donor, temperature, speed of agitation, catalyst loading etc. Also without ultrasound experiment was performed to check the role of ultrasound under best suitable conditions.

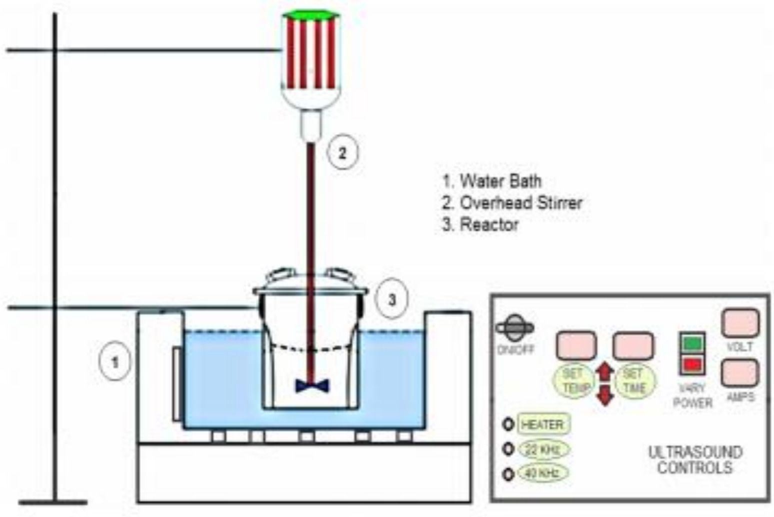

Fig.1. Experimental setup for ultrasound-assisted CTH of oil

IV. MATERIALS & METHOD

4.1 Solvent Selection. Depending on the nature of the substrate and donor, solvent selection plays an important role in CTH reaction [25].Water is the most suitable solvent for CTH. Generally higher water content results in better contact between hydrogen donor & oil which gives lower final acid value. Different values of water quality such as 25, 50, 75 & 100 mL with 150 W ultrasonic power 22 kHz frequency used to dilute the hydrogen donor which results reduction in final iodine value also[4]. Increase in the amount of water content from 25 to 75 mL with reaction time of 2 hours gives higher reduction in iodine value of sunflower oil from 98.45 to 84.14 g/100 g of oil[10]. Much aqueous content may lead to much intense cavitation. Tike & Mahajani reported similar results for soybean oil with CTH process[1]. 50 mL should be the appropriate water quantity for the dilution of hydrogen donor.

4.2 Effect of hydrogen donor type. The effect of various hydrogen donors was observed on CTH of different oils like potassium formate, sodium formate, ammonium formate & formic acid[26][10]. Generally formic acid & its salts or secondary alcohols have been reported as an efficient hydrogen donor with respect to ease of handling. Potassium formate forms mixture of stronger alkali salts like K_2CO_3, $KHCO_3$ etc which can affected on performance of palladium catalyst due to the deposition of palladium hydride on surface. As per the previous experiments ammonium formate gives minimum possible iodine value & hence can be reported as the best donor type[1]. It is also preferred over the formic acid salts as it decomposes into carbon dioxide & ammonia as a byproduct of reaction which can be washed out with water easily. Also gaseous ammonia can be recycled back for the reaction. The additional benefit of ammonium formate is due to the higher solubility in water which can give “greener” approach for hydrogenation.

4.3 Catalyst type & selection. Typically nickel catalyst is used in the hydrogenation process of edible oils[23]. Other catalysts like copper, platinum can also use for hydrogenation of oils. The temperature required for hydrogenation using nickel catalyst is about 160-200^{0}C. Sarnaik et al. reported that palladium on carbon as the best catalyst for CTH of oil[10][14], due to ease of separation of products & recovery of catalyst. The effect of Pd/c catalyst loading was investigated by Sancheti et al. on soybean oil [4]. It allows the reaction to work at much lower temperature & also speeds up the rate of CTH reaction[20][27]. At the initial stages of the reaction, the selectivity was significantly higher than conventional hydrogenation process[17]. This reduces the amount of energy used in reaction which is quite good for sustainable development.

4.4 Ultrasonic parameters & its effects. For CTH process the ultrasonic power range should be 50 to 200 W & with two frequencies as 22 & 40 kHz[3]. For the mass transfer resistances in the heterogeneous system we should apply the lower frequency parameters as it gives better efficacy which is attributes to higher physical effects. At lower frequency conditions the bubble have adequate time to grow & to increase the intensity of cavitational activity[21]. Catalytic procedures by using water solvent assisted by ultrasound and/or hydrodynamic cavitation are ecofriendly with milder conditions, shorter reaction times and higher yields. Sonochemical processes can reduce the formation of hazardous by-products, the generation of waste and also produce energy savings[18][22]. Mostly the ultrasonic equipments are available at constant frequency operations. The formation of higher amount of cavitation bubbles in the form of cloud may affected on reaction & conversion[19]. The effect of power was also studied by Sarnaik et al. at 22 kHz frequency with different ultrasonic power such as 50, 100, 150 & 200 W for sunflower oil[10]. Also Sancheti et al. reported that for soybean oil conversion increased drastically over the range of 50-100 W & beyond 100 W lower conversion was observed to poor propagation of ultrasound waves through the reaction mixture[4].

4.5 Effect of temperature. In conventional reaction system increase in temperature increases the kinetic rate constant. For CTH process different temperatures as 30^0C, 45^0C, 60^0C & 75^0C has been observed. At higher temperature cavitation becomes easier & net collapse intensity is lower giving finally reduced intensification effects[16]. Hadiah et al. have reported the increasing temperature effect for CTH of candlenut oil[24]. Minimum iodine value is obtained with high temperature as the increase in temperature increases vapor pressure of liquid. Marginal difference was observed for the temperature between 30^0C to 40^0C & hence 30^0C is the appropriate temperature with lower energy input for CTH.

V. COMPARISON BETWEEN CONVENTIONAL AND ULTRASOUND-ASSISTED APPROACH

In conventional vegetable oil hydrogenation process the reaction temperature is about 180-200^0C. But in ultrasound CTH approach we can operate the reaction at minimum temperature at 30^0C approximately. Tike & Mahajani reported that using 30^0C in the conventional process did not observed any change in final iodine value of oil[1]. Thus ultrasound use gives higher reduction in iodine value at a much lower temperature, which can give us significant less operating cost with ease of handling & safer operation. Ultrasonic approach also reduces the mass transfer resistance favoring higher rate of reaction[15]. Generally hydrogenation reactions poses a big fire hazard due to the utilization of flammable reagents and solvents. Such reagents which is highly flammable and can ignite solvents and hydrogen. It is quite dangerous after having been used for the hydrogenation reactions. The presence of hydrogen gas increases the danger of explosion. CTH is the good alternative for these conventional hydrogenation process as we use hydrogen donor instead of hydrogen gas.

VI. ADVANTAGES

Economical process:
Catalytic transfer hydrogenation, is cheaper and safer process because no free hydrogen gas is used and because it does not require a special type of reactor, or special gas handling auxiliaries & supervision. Solvent used in CTH process is cheap & easily available which gives intrinsic simplicity to the process.

Increase in selectivity:
The advantage of using hydrogen donor solvent is to stabilize the free radical in the biomass liquefaction and yielding a higher product conversion. The use of heterogeneous catalyst that provide advantage of comparatively easy recovery and recycle.

Less reaction time:
Use of ultrasound can give intensified processing (lower reaction times) under mild reaction conditions and with minimum side reactions resulting in higher selectivity and yields for the specified product. Process intensification approaches with possible benefits of reduced reaction times only up to 2 hours and temperatures can make the method efficient and economical.

Reduction in Iodine value:
Increasing dilution of hydrogen donor like formate solution using higher water resulted in higher reduction within the iodine value (IV) confirming higher extent of hydrogenation.

Low temperature/ pressure reaction:
Use of ultrasound offers immense potential as process intensification approach supported the physical and chemical effects generated thanks to cavitation induced by the passage of ultrasound. Using this, excellent progress of hydrogenation was observed even at 30^0C which is much lower compared to the conventional approach. The CTH technique doesn't require high-pressure operation and elaborate precautionary method, utilized in conventional catalytic hydrogenation.

Ease of handling:
Besides good selectivity and short response time, this method offers safe and straight forward handling. The CTH method doesn't require eventually hazardous pressurized H_2 gas nor elaborate experimental setups. The hydrogen donors are readily available, inexpensive, and easy to handle, transport and store.

Greener approach:
Due to the use of hydrogen donor there is no formation of toxic compounds & the all products are biodegradable. This represents the greener approach as there is no any type of pollution will occur which is more beneficial to the environment.

Low energy consumption:
The major side product can be recycled, and the catalysts that are involved usually are readily accessible and not sensitive. Reaction time required is less. With reference to yield and purity, the CTH methods were very similar and superior to the economic method.

VII. DISADVANTAGES

• Although palladium is an efficient catalyst, but the high price of palladium becomes an obstacle for CTH. Also palladium is toxic, therefore further CTH research is required to seek out a less expensive but effective catalyst that would work on moderate temperature and pressure.
• Compared to CTH, conventional method has lower costs and generates significantly less waste.
• Homogeneous catalyst offer disadvantages of separation of catalyst & also recover & recycle issue.

VIII. CONCLUSION

Catalytic transfer hydrogenation seems to be a promising alternative method for hydrogenation of oil. The drawbacks of a conventional hydrogenation process such as longer reaction time, poor conversion, yield of desired products, higher requirement of energy, toxic reagents, and higher temperature and pressure conditions lead to unsafe and uneconomical ways of processing which can be avoided by the use of CTH. The use of ultrasound in this process presented an intensified and greener processing approach based on the requirement of lower temperatures and also gave increased iodine value reduction. The CTH provides an effective & economical manufacturing option to small & medium scale manufacturers & industries who do not have experience and system dealing with high-pressure hydrogenation operations.

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