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Review Paper

Sub-critical water as a green solvent for production of valuable materials from agricultural waste biomass: A review of recent work

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ABSTRACT: Agricultural waste biomass generated from agricultural production and food processing industry are abundant, such as durian peel, mango peel, corn straw, rice bran, corn shell, potato peel and many more. Due to low commercial value, these wastes are disposed in landfill, which if not managed properly may cause environmental problems. Currently, environmental laws and regulations pertaining to the pollution from agricultural waste streams by regulatory agencies are stringent and hence the application of toxic solvents during processing has become public concern. Recent development in valuable materials extraction from the decomposition of agricultural waste by sub-critical water treatment from the published literature was review. Physico-chemical characteristic (reaction temperature, reaction time and solid to liquid ratio) of the sub-critical water affecting its yield were also reviewed. The utilization of biomass residue from agriculture, forest wood production and from food and feed processing industry may be an important alternative renewable energy supply. The paper also presents future research on sub-critical water.

Keywords: *Agricultural waste, Bio-fuel, Phenolic compounds, Sub-critical water treatment (SCW), Water soluble sugars*

INTRODUCTION

By-products generated from agricultural production and food processing industry are abundant biomass, such as corn straw, rice bran, corn shell, potato, durian and mango peel etc. Existing environmental laws and regulations pertaining to the pollution from agricultural waste streams by regulatory agencies are more stringent and the application of toxic solvents during processing has become public concern. Due to these reasons, there is an urgent need to identify alternative ways to properly treat the waste materials to recover valuable resource (phenolic compounds, water soluble sugars, bio-fuel, organic acids etc.) from the biomass residues, which have pharmaceutical, cosmetics and bio-fuel values (Deng *et al.*, 2012). The utilization of the fruit wastes as renewable energy sources may be financially and environmentally attractive. However, such facts are still to be established through research.

Several methods for material extraction are categorized as conventional and non-conventional. Valuable compounds from plants, waste residues and soil toxic contaminants can be produce and/or recovered using conventional extraction methods. Extraction efficiency of these methods largely depends on the extracting capacity of the extraction solvents and temperature during extraction (Azmir *et al.*, 2013). The most popular and widely use methods are Maceration (Vongsak *et al.*, 2013) and Soxhlet extraction (Ruiz-montañez *et al.*, 2014).

The major drawbacks of conventional extraction techniques are long time, expensive, use of large quantity of organic solvent, poor extraction selectivity and generation of toxic organic waste (Azmir *et al.*,

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2013; Mohammad and Fereshteh, 2007). To establish environmentally benign methods for materials recovery, Researchers have made great efforts and introduced new and promising extraction techniques to overcome challenges faced during extraction methods. These techniques include supercritical fluid extraction (Fornari *et al.*, 2012), Sub-critical water treatment (Zhu *et al.*, 2013b), pulsed electric field assisted extraction (Suan, 2013), microwave-assisted extraction (Zeng *et al.*, 2010), pressurized liquid extraction (Teo *et al.*, 2010), enzyme-assisted extraction (Suan, 2013) and ultrasound assisted extraction (Yang *et al.*, 2011).

Sub-critical water treatment (SCW) treatment technology is gaining prominence as a method of valuable material recovery. The SCW is inexpensive, take short time, use non-toxic solvent (water), good selectivity and is considered as ecofriendly technology (Abdelmoez *et al.*, 2014). The SCW is defined as the water that maintains its liquid state at temperatures between its boiling point 100°C and its critical point 374°C under adequate pressure (Yoshida *et al.*, 2014; Abdelmoez *et al.*, 2007). The SCW is also called superheated water or pressurized hot water (Yoswathana and Eshtiaghi, 2013). At these conditions SCW possesses two distinctive characteristics: first its dielectric constant decreases, which make it to act as solvent for hydrophobic matters and secondly high magnitude of ion product at elevated temperature (Adachi, 2009).

The aim of this study is to present a comprehensive review of the principles and instrumentation of SCW treatment technology as well as its application in the production of bio-fuel, water soluble sugars and phenolic compounds extracted from agricultural waste.

Sub-critical water (SCW) treatment

Considerable quantity of extractable components from diverse biomass could be obtained by utilizing pressurized hot water. In recent years, there has been an increasing volume of literature on SCW for its wide range of application in the field of environment due to its advantage of being green, environmentally friendly technology, higher quality of extraction product, cost effective and less time consuming in preference to other traditional solvent extraction methods (Ravber *et al.*, 2015; Tunchaiyaphum *et al.*, 2013; Abdelmoez *et al.*, 2011). Furthermore, SCW process can be carried out in dynamic mode where water flows continuously through the solid sample. The static mode is called batch process, where both water and the sample are enclosed in the batch reactor, whereas the combination of the two process is known as dynamic-static (Jintana and Shuji, 2008). The SCW region is shown in Fig. 1.

The extraction process is normally conducted at a temperature range from 100 to 374°C under sufficient pressure that maintains the water liquid state (Yoshida *et al.*, 2014).

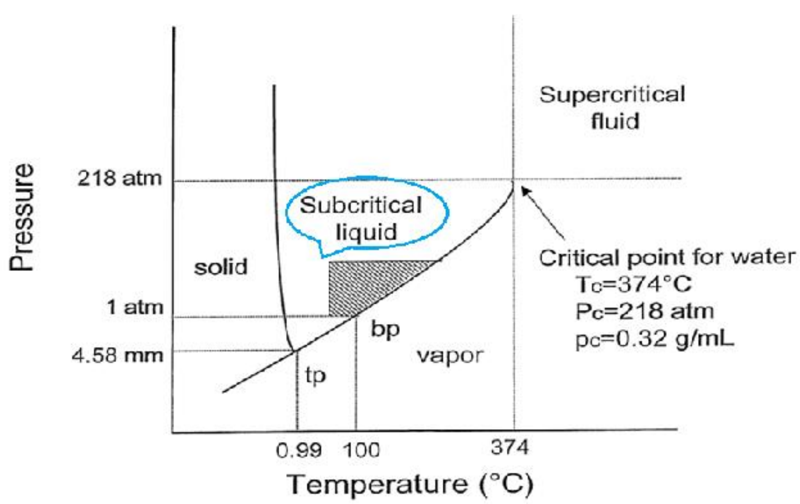

Fig. 1: Water phase diagram as a function of pressure and temperature (Adapted from Khajenoori, 2013)

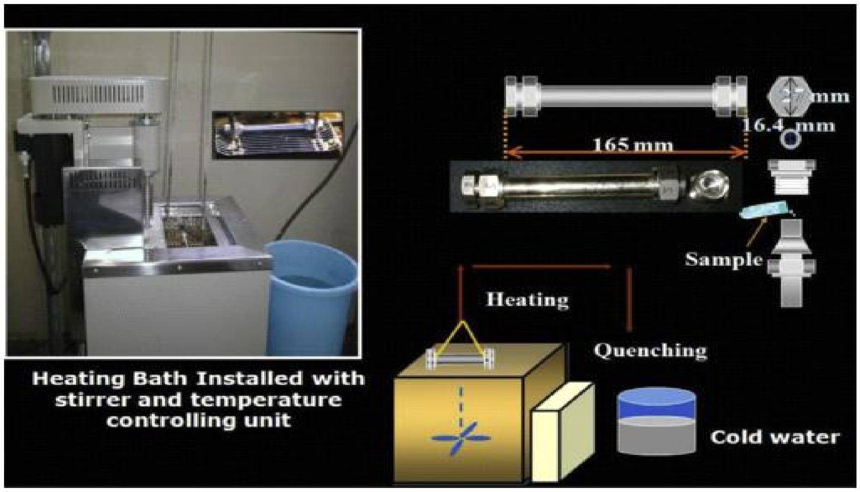

Fig. 2: Sub-CW treatment Apparatus (Abdelmoez *et al.,* 2014)

A Batch mode SCW treatment apparatus set up (Fig. 2) is quite simple; consisting of standard stainless steel batch reactor (SUS316, id. 16.5 mm×150.4 mm) from Swagelok & Co.

The required quantity of sample and distilled water is placed in the reactor, and then argon gas is used to force the air out of the reactor. The reactor is capped and tightened properly, then dipped into a heated oil bath (Thomas Kagaku Co. Ltd.) for reaction at temperatures of 100 to 180°C and in preheated salt bath (Thomas Kagaku Co. Ltd.) of 200-360°C for a desired reaction time. After the preferred reaction time is reached, the reactor is taken out from the heating bath and immediately immersed in cold water at ambient temperature (Abdelmoez *et al.,* 2014). Steam table is use to determine the treatment pressure.

Physicochemical Properties of Water

Water at ambient temperature is a polar solvent with a dielectric constant, ε, of 79.9, constant ion product and a density of 1000 kg/m^3, but when water is heated to high temperature its hydrogen bonds break down causing its dielectric constant to fall (Cheigh *et al.,* 2015; Lu *et al.,* 2014). The important properties of water at SCW state are briefly given below.

Dielectric constant

Dielectric constants (ε) indicate the affinity of water acting as a material reaction media. Singh, (2011) reported that at room temperature and pressure the dielectric constant of ethanol, methanol and pure water are 27, 32.5 and 79.9 respectively. As can be seen from Fig. 3 when water is heated up to 250°C and it maintains its liquid state with an increased pressure of 5Mpa the dielectric constant of the water decreases from 79.9 to 32.5 and 27, which is exactly same as the dielectric constant of methanol and ethanol respectively (Singh, 2011; Amashukeli *et al.,* 2007). A low dielectric constant allows SCW to dissolve organics compounds.

Ionic product

It is believed that when water acts as acid or base, it gives and takes protons. The reaction of water with similar substances produced basic hydroxide and acidic hydronium ions. Fig. 4 presents the ionization constant of water in SCW region, the ionic constant (Kw) of water increases with the increased reaction temperature and is about three times higher in magnitude than at room temperature (Pourali *et al.,* 2009a). The ion product of water is defined as $Kw = [H^+] [OH^-]$ concentration. The high ionization product constant allows SCW to provide an acidic medium for hydrolysis reaction, it makes the water to behave as an acid catalyst (Carr *et al.,* 2011).

Parameters affecting SCW treatment

The main process parameters affecting the extraction efficiency of SCW treatment includes reaction temperature, pressure, reaction time, solid to water ratio (Ndlela *et al.,* 2012), samples particle size, pH, solute

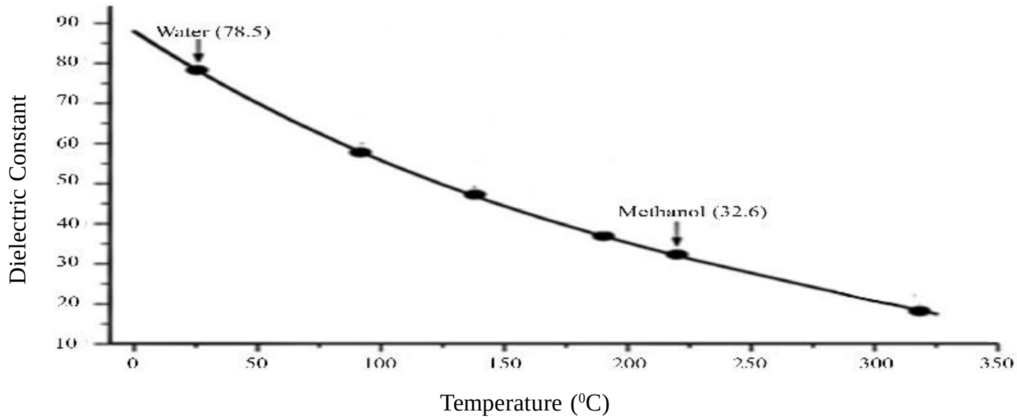

Fig. 3: Behavior of water dielectric constant at 20 MPa (Adapted from Amashukeli *et al.,* 2007 and Singh and Saldaña, 2011)

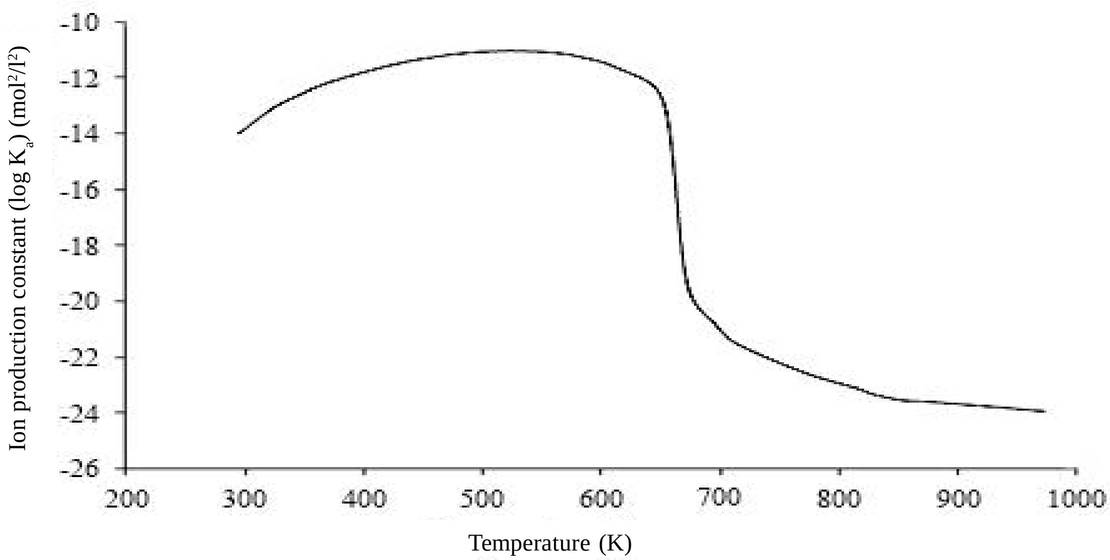

Fig. 4: Effect of temperature on ionization constant of water (Adapted from Pourali *et al.,* 2009)

characteristics, addition of a surfactant and flow rate (Khajenoori *et al.*, 2009). Three parameters are discussed in this review.

Effect of Temperature

Reaction temperature is one of the most important factors affecting the SCW treatment efficiencies, because temperature significantly affects physicochemical properties of water (Jintana and Shuji, 2008). Researchers have shown that, increase in the treatments temperature remarkably increase mass transfer rate and high solubility of bioactive compounds. As the temperature increases, its viscosity and surface tension of the extraction solvent is decreased (Asl and Khajenoori, 2013). Therefore, SCW treatment must be carried out at the maximum allowable temperature. Asl and Khajenoori, (2013) reported that, increasing the extraction temperature beyond the permitted value might also cause degradation of essential compounds. Moreover, the effect of temperature varies for different materials, and is influence by the concentration of the bioactive compound in the product (Singh and saldana, 2011).

Table 1 presents the optimum reaction temperature and time for the extraction of valuable resources from agricultural waste. Increasing reaction temperature from 160 to 180°C in the decomposition of mango peel waste, increases total phenolic compounds enhancement from 24.75 mg Gallic acid equivalent (GAE)/g to 30.62 mg GAE/g (Tunchaiyaphum *et al.,* 2013). Similarly Singh and saldana, (2011) investigated the effect of extraction temperature on potato peel and found that higher concentrations of phenolic compounds were recovered at temperatures from 140 to 180°C. However, further increase in the reaction temperatures from 180 to 240°C lowered the yield of recovered phenolic compounds. This could be attributed to sample pyrolysis above 180°C which resulted into phenolic compounds degradation (Cheigh *et al.*, 2015).

Additionally, temperature also has great influence on valuable materials recovery from waste. Due to the fact that chemical reactions such as oxidation and hydrolysis activity significantly increase and some thermally labile compounds may be degraded after being released from the sample matrix (Jintana and Shuji, 2008)**.** Increasing treatment temperature from 100 to 220°C increased the quantity of total phenolic compound extracted but at temperature above 220°C it was found that the of phenolic compounds degraded to form other compounds (Alvarez and Saldaña, 2013). Maximal recovery of valuable materials has optimum temperature range from 100-180°C (Singh, 2011)**.**

Effect of reaction time

Time is another factor that influences the extraction performance of SCW hydrolysis. However, reaction temperature and nature of the sample have greater influence on the extraction (Jintana and Shuji, 2008). He *et al.,* (2012) investigated the effect of extraction time on total phenolic contents from pomegranate seeds (*Punica granatum L.)* at 140°C and solid to water ratio 1:40. They found that 1510.0 mg/100g of phenolic compound within 30 minutes and when the extraction time was increased to 120 minutes, 1890.0 -mg/100g of phenolic compound was recovered. Thus 30 minutes is the optimum extraction time since 80% of 1890.0 mg/100g at 120 minutes was recovered. On the other hand, increased temperature of the treatment lowered the treatment time required for material recovery (Jintana and Shuji, 2008).

Tunchaiyaphum *et al.,* (2013) studied the effect of extraction time for recovery of phenolic compounds from mango peel waste with solid: water (1:40) at 180°C. They reported increase in yield from 13.78 to 35.96 mg GAE/g

Table 1: Optimum reaction temperature and time for extraction of valuable material from diversified biomass

Sample	Desired product	Experiment. Temp. (°C)	Optimum Temp. (°C)	Optimum Time (min)	Source
Cotton seed	Oil	180–280	270	30	(Abdelmoez *et al.,* 2011)
Potato peel	Glucose	140-240	240	15	(Alvarez and Saldaña, 2013)
Japanese red pine wood	Organic acid product	-	270	10	(Asghari and Yoshida, 2010)
M.Chamonilla.	Essential oils	100-175	150	120	(Khajenoori, 2013)
Corn stalks	Fermentable hexose	180-392	280	27	(Zhao *et al.,* 2009 check a or b)
Wheat straw	Fermentable hexose	-	280	54	(Zhao *et al.*, 2009 check a or b)
Cellulose	Oligosaccharides	-	380	16	(Zhao *et al.,* 2009b)
Wheat straw	Reducing sugars.	170-210	190	30	(Abdelmoez *et al.*, 2014)
Fish proteins	Amino acid	180-320	260	30	(Cheng *et al.*, 2008)
Zataria Multiflora Boiss	Essential oils	100-175	150	150	(Khajenoori *et al.*, 2009)
Bagasse waste	Reducing sugars	200-240	240	2	(Zhu *et al.,* 2013) check a or b
Defatted rice bran	Sugars and proteins	200-260	200	5	(Hata., 2008) Check a or b
Jojoba seed	Oil	180-260	240	30	(Yoshida *et al.*, 2014)

DW when the reaction time was increased from 30 to 90 minutes. But prolonged reaction time from 90 to120 minutes gave very low quantity, which is due to the decomposition of phenolic compounds (Wang *et al.*, 2014).

Effect of Solid to water ratio

Solid to water ratio is another important parameter that affects SCW extraction efficiency and recovery. Table 2 shows the optimum solid to water ratio reported by previous researchers. Mango peel was investigated by Tunchaiyaphum *et al.*, (2013) for the production of bioactive compound using SCW. The effect of solid to liquid ratio (1:10 and1:50) on the total phenolic compounds production was determined. They found at solid to liquid (1:50), the total phenolic increased to the highest yield (40.86 mg GAE/g). In a similar manner Abdelmoez *et al.*, (2014) has performed a study on the effect of solid to liquid ratio on exraction of essentional oil from wheat straw using SCW hydrolysis. They reported that using a ratio of 1:6 of sample to water, higher amount of extract was recorded. Large volume of water can easily dissolved the extract than little quantity of water (Cardenas -Toro *et al.*, 2014; Tunchaiyaphum *et al.*, 2013). At the point when the water volume was low, water and solid particles would simply inundated, resulted in the low extraction efficiency (Gong *et al.*, 2013). Relatively, there is certain level where high volume of the solvent decreases the quantity of extract (Gong *et al.*, 2013).

Valuable materials production from agricultural biomass

Total soluble sugars and reducing sugars

The SCW treatment technology for the conversion of lignocellulosic biomass has emerged as a better and green alternative method for the production of soluble sugars from agricultural residues. Large quantities of residual biomass are produced from agricultural production, such as rice bran, wheat straw, corn shells, sugarcane bagasse, microalgae, durian peel and other fruits processing industry waste product (Viganó *et al.*, 2014). The process is aimed at utilizing the waste to produced raw materials for new product and reduction in waste stream volume. The soluble sugars produced have cosmetics, fermentation and food applications. Wiboonsirikul *et al.*, (2008) investigated the production of fermentable sugars from defatted rice bran using SCW at reaction temperature of 180 to 280°C and 5 minutes reaction time. They reported significance enhancement of sugars at 200°C but recovery decreases with increasing reaction temperature and time. The most suitable temperature for sugar recovery is around 200°C. At these temperatures SCW possess higher hydrolysis power. Production of soluble sugars from rice bran was also reported by Pourali *et al.*, (2010). They applied SCW to decomposed rice bran under different reaction temperatures and timing in a batch reactor. They observed higher amount of water soluble sugars (215 glucose equivalent mg/g dry samples) at 220°C requiring 3 minutes reaction time. The soluble sugars produced were in oligomers and monomers. Similarly, Shimanouchi *et al.*, (2014) also recovered reducing sugars from *Carya Cathayensis Sarg* Peel (CCSP) under SCW condition at different reaction temperatures. They concluded that, the optimal conditions for production of reducing sugar from CCSP were 190°C and 60 minutes for reaction temperature and time, respectively. Agricultural waste is largely composed of hemicelluloses, lignin and cellulose which can be decomposed using SCW hydrolysis to water soluble sugars and other valuable resources (Unhasirikul *et al.*, 2013).

Recently, Prado *et al.*, (2014) subjected defatted grape seed, coconut husk and pressed palm fiber waste residue from food industry to a SCW hydrolysis

Table 2: Effect of solid to water ratio on extraction

Sample	Material extracted	Solid water ratio	Optimum ratio	References
Pomegranate seeds	PC	1:10–1:50	1:40	(He *et al.*, 2012)
Mango peel	Bioactive compound	1:10–1:50	1:50	(Tunchaiyaphum *et al.*, 2013)
Cotton seed	Essential oil	1:1-1:2	1:1	(Abdelmoez *et al.*, 2011)
wheat straw	Value added product	1:1-1:7	1:6	(Abdelmoez *et al.*, 2014)
Jojoba seed	Oil	1: 0.5-1:3	1:2	(Abdelmoez *et al.*, 2012)

and produced fermentable sugars. The study was conducted using a 50 ml semi-batch reactor at reaction temperature range from 208 to 257°C for 30 minutes. The increase in reaction temperature increased the yield of total reducing sugars from all the raw materials. The maximum soluble sugars recovered were 11.9%, 11.7% and 6.4% from pressed palm fiber, coconut husk and defatted grape seed residue, respectively. The researchers concluded that the low yield of the fermentable sugars from the defatted grape seed could be attributed to its low content of hemicellulose and cellulose. Therefore, defatted grape seed is not potential biomass for recovery of reducing sugar when compared with other raw materials such as coconut husk, pressed palm fiber, 30% from rice bran (Wiboonsirikul *et al.*, 2007) and 61.5% from sugarcane bagasse (Zhu *et al.*, 2013a). The agricultural biomass from fruit residues serves as inexpensive and renewable sources of fermentable sugars and other value added materials.

Bioethanol/ biodiesel/ biofuel

Biomass is considered to be the largest and low cost source of renewable energy. Particularly, agricultural waste biomass such as corn stalks, peels, seeds residue, sugar cane bagasse, woods residue and many more, which have been reported to be decomposed for the production of bioethanol/biodiesel under SCW conditions (Shimanouchi *et al.*, 2014; Uddin *et al.*, 2010). The production of biofuel from these residues would be a favorable, promising and environmentally friendly alternative method. Nowadays, there are more concerns about renewable energy resources for biofuel productions. Due to its minimal environmental pollution (biodegradable), less greenhouse gases emission, low-cost, technological advantages and renewable nature as compare to the normal conventional petroleum-derived fuels (Demirbas, 2009). Bioethanol chemically is C_2H_5OH or EtOH and is also known as ethyl alcohol, and is largely used to fuel light duty vehicles. On the other hand, biodiesel is the alternative diesel fuel which is largely used to drive heavy duty vehicles. The SCW has wider applications, such as decomposition and hydrolysis processes due to its unique properties (Kruse and Dahmen, 2014; Pourali *et al.*, 2009b). Ravber *et al.*, (2015) have shown that sunflower seeds were decomposed to bio oil and water soluble extract. Also Woo *et al.*, (2014) have reported the production of biodiesel from Jatropha carcass seed kernels under SCW conditions. Likewise, Abdelmoez *et al.*, (2012) extracted oil from jojoba seed for bio-fuel production using SCW hydrolysis. They reported the optimum conditions of SCW hydrolysis for the extraction of bio base oil from jojoba to be 240°C, 30 minutes and 3mm of reaction temperature, time and particle size, respectively. Another advantage of SCW extraction process is that it does not require any wet waste dewatering before the decomposition process. This reduces considerable amount of energy requirement for drying process, because water is used as a solvent in the extraction process (Ponnusamy *et al.*, 2014; Reddy *et al.*, 2014). The crude oil extract obtained from the SCW decomposition is converted to biodiesel by transesterification process (Ponnusamy *et al.*, 2014). Transesterification is regarded as one of the most efficient treatment methods to reduce crude oil extract viscosity by making it more suitable as a biodiesel (Nazir *et al.*, 2013). However, the parameters that affect biodiesel yield from the transesterification are reaction time, catalyst, reaction temperature (Zhang, 2014), moisture and mixing intensity (Nazir *et al.*, 2013).

Phenolic compounds

Fruits, plants, and vegetables residue contain numerous bioactive active substances, such as ascorbic acid (vitamin C), vitamin E and phenolic compounds (antioxidant) (Cheigh *et al.*, 2015). The consumption of these substances is an essential health-protecting factor. Evidence for their role in preventing cancer and cardiovascular diseases is emerging (Garcia-Salas *et al.*, 2010). In recent years interest in the production of phenolic compounds from agricultural residual biomass is increasing. Recently, SCW treatment has been successfully applied in the advancement of extraction methods for phenolic compounds from fruit peel, shell, seed, and food matrices among others. These studies have shown that the extraction of phenolic compounds is highly effective when SCW technology is used. The study by Singh and Saldaña, (2011) demonstrates the utility of SCW extraction production of phenolic compounds from potato peel. It was found that, 81.83 mg/g of phenolic compounds were recovered at 180°C within 30 minutes reaction time as compared to 46.59 mg/g in 3 hours reaction time using methanol. In a similar study Tunchaiyaphum *et al.*, (2013) produced phenolic compounds from mango peel under SCW conditions. Highest phenolic contents obtained was 50.25 mg/g at 180°C, decomposition time of 90 minutes, 1:40 solid water ratio and pH 4 while using soxhlet extraction techniques where the extraction time was 120 minutes, which is higher than SCW. The researchers suggested the viability of replacing the conventional methods with SCW technology. According to Rangsriwong *et al.*, (2009) SCW has been shown to be a promising and most effective method for phenolic compounds extraction from *Terminutesalia chebula Retz* fruits. In this case, comparison was made between SCW and Soxhlet extraction methods. The result revealed that, SCW hydrolysis required only 37.5 minutes to recovered highly substantial amount of phenolic compounds while soxhlet extraction method required more than 2 hours reaction time to achieve maximum yield of phenolic compounds. Their findings were supported by Sasaki and Goto, (2008). In addition Budrat and Shotipruk, (2009) decomposed bitter melon (*Momordica chianti*) using SCW hydrolysis aimed to produce phenolic compounds. The extracted phenolic compounds have strong antioxidant activity.

CONCLUSION AND FUTURE PERSPECTIVE

The future perspectives presented here will serve as the conclusions of the present review on the subject matter. The utilization of biomass residue from agriculture and forest wood production and from food and feed processing industry could be an important alternative renewable energy supply. However, future of production of value added materials from agricultural waste residue using SCW treatment technology is undoubtedly promising. This can results in high quality products as well as lower production cost and higher efficiency. In addition, this can also lead to the viable valuable materials recovery at industrial scale. It is important from economic, ecological and resource point of view that global agricultural and food processing waste streams are evaluated for their potentials as sources for several bioactive compounds and/or renewable energy precursor.

Additionally, the use of vegetables, fruit and forest residue as source of renewable energy have been considered the best alternative solution for substituting the petroleum base oil-dependency dilemma, the increasing demand and investment in biofuel development has gained momentum. Moreover, utilizing these waste provide a path way through which pollution problems as a result of poor disposal of food industry residue will be alleviated.

The review of literature revealed the experiments were successfully conducted in the laboratory or at pilot scale, but still there is a need to explore the potential further application of the SCW technology at large industrial scales. It is important to recall that SCW is performed using water as extraction solvent which is green, safe, cheap and readily available while in the traditional conventional methods, toxic organic solvents are usually employed which are expensive, long time consuming and contribute to environmental pollution. The SCW could completely decomposed cellulose and hemicellulose part of biomass sample in a very short reaction time compared to the organic solvent extraction methods. Finally, it is recommended to develop the marketing strategies, by the stakeholders to their client about the advantages and benefits of applying SCW to recover value added resources from food wastes.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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