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Potentials of Citrus Peel Waste Valorisation for Green Diesel Production: A Mini Review

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The utilisation of fossil derived diesel for running diesel-based transportation has caused anthropogenic Green House Gas (GHG) emission. Environmental challenges seen in the form of acid rain and global warming are attributed to the high release of these emissions. Consequent upon these impacts, the application of renewable fuel for diesel engine operation is a good option to aid reducing GHG emissions. Citrus peel, a biomass waste produced after extracting the most valuable fruit juice, contains oil with fuel-like properties that can be explored as biofuel. The presence of limonene in citrus peel acting as a microbial growth inhibitor, limits the decomposition of citrus peel waste which causes generation of bad odour over a long period with tendency for aiding disease outbreak. Citrus peel waste valorisation for green diesel production presents a double fold benefit. It contributes in effective waste management of citrus peel biomass waste and provides environment friendly green sustainable energy source in support of the United Nations Sustainable Development Goals number 7 and 13. This study aims to present a mini review on the potentials of citrus peel waste valorisation methods for green diesel production. Supercritical Fluid Extraction Method was found to be the method with potential for optimum CPO yield for green diesel production. Some fuel properties of CPO relative to diesel varies with wide margin, a challenge to be remedied by hydrotreatment for the CPO to behave similar to conventional diesel. The catalytic hydrotreatment may be the new direction towards a cleaner and greener renewable diesel synthesis.

1. Introduction

Environmental impact of increased Green House Gas (GHG) emissions from diesel engines running on fossil-derived diesel fuel is becoming an issue of global concern, compelling the United Nation to put in place stringent policies on GHG reduction for nations to comply with (Tan et al., 2021). A change to the usage of environmentally friendly biofuels, such as green diesel, will be the solution to this issue (Fatt et al., 2022). The use of green diesel in diesel engines for transportation, industrial heating, and other utility purposes will reduce GHG emission, which is currently a threat to our living planet. Green diesel is a renewable, biodegradable, and non-toxic fuel alternative to fossil-derived diesel (Alsultan et al., 2021).
According to Abatzoglou et al. (2007), every m^3 of fossil derived diesel burnt in engine for transportation today, emits an equivalent of 2.5 t of CO_2 and replacing just 25 % of fossil diesel by green diesel will considerably reduce the GHG emission by about 10 Mt per annum. The use of biofuel has been on since Rudolph Diesel developed his diesel engine and used peanut oil to test it in 1900 (Balat, 2006). However, the use of such non-conventional fuels never really took off due to the availability of cheap fossil fuel until recently as reserves continue to deplete, fuel prices rise, and stricter government regulations on GHG emissions being enforced.
Citrus with an annual production of 110–124 Mt, is the most widely produced fruit crop in the world with Asia (44 %), Europe and Mediterranean (20 %), South America (18 %) and North and Central America (13 %), Africa

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(4 %) and Oceania (1 %) (Mahato et al., 2021). About 50 % of the fruit is non-edible and after extracting the edible fruit juice, the peels are thrown away as garbage which constitute nuisance in the environment. Instead, the peels can be explored to produce diesel-like oil which can be processed to renewable diesel. The presence of limonene in citrus peel acting as a microbial growth inhibitor, limits the decomposition of citrus peel waste, causing bad odour generation over a long period with tendency for aiding disease outbreak. About 54 Mt of citrus peel waste is produced each year by food processing sector (Teigiserova et al., 2021), which includes juicing and canning, and has the eminent potential to be used as a raw material in bio-refineries to make pectin, citrus peel oil, and bioethanol (John et al., 2017).
Citrus peel from citrus fruit (orange, lemon, mandarin, grapefruit, tangerine, etc) contains oil in the flavedo portion of the peel located at about 1 mm depth from the fruit peel surface. This oil with a yield of between 1.0 – 10.5 % (depending on the cultivar, extraction method, soil and climatic condition of the biomass citrus fruit source), is a mixture of mainly hydrocarbon monoterpenes (Teigiserova et al., 2021). Utilization of this peel will serve dual benefits of waste management and biofuel production in support of the United Nations Sustainable Development Goals number 7 and 13. Thus, it is the objective of this study to provide a review on the potentials of citrus peel waste valorisation methods for green diesel production. It will unveil relevant prospects imbedded in citrus peel waste valorisation for GHG emission control, energy security and sustainable environment.

2. Fuel properties comparison of citrus peel oil

Citrus peel oil is a mixture of many compounds with limonene being predominant with percentage composition 96.925 %, 92.7 % 77 % from the cultivars of Vietnam, China and Mexico shown in Table 1. Limonene is the major component of CPO that gives it fuel attributes. The compounds present in the oil were identified by comparing the various retention time from the GC-MS chromatogram of the oil sample and compared with those reported in other literatures and the standard database of the National Institute of Standards and Technology (NIST) spectral library. Citrus peel oil composed of 68 - 98 % limonene (Ozturk et al., 2019). Physicochemical properties of citrus peel oil as reported by (Ashok et al., 2017) and shown in Table 2, tends towards that of conventional diesel and will require little enhancement to modify the properties and make it a canonical of the fossil-derived diesel.
From the physicochemical properties of citrus peel oil (LPO) shown in Table 2, it could be deduced that the density and calorific value of the oil are close to that of diesel and B10 fuel. The percentage difference of its density and calorific value from that of diesel is just 1.26 % and 9.45 %. While the percentage difference of its flash point, cetane index and kinematic viscosity from that of diesel are so significant being 41.93 %, 72.53 % and 70.80 %, which pose a great challenge to its use as diesel engine fuel. Furthermore, the percentage difference of carbon, hydrogen and oxygen composition of the oil relative to diesel are 6.94 %(higher), 27.77 % and 79.23 % of which the most important expected to play critical role is the composition of hydrogen that need to be improved upon. Similarly, percentage property variation of CPO relative to B10 fuel tough the same line. This percentage property variation shows that CPO can be made to behave like a conventional diesel and burn efficiently in diesel engines when modified for the properties to be within the range of a conventional diesel. This oil modification (property enhancement process) is the green diesel production process that can be achieved through catalytic hydrotreatment of the oil.

Table 1: Composition of CPO sourced from different cultivars and countries (%) (Products et al., 2019)

Peak	R.T. (minutes)	Name	Vietnamese Calamondin	China *C. bergamia*	Mexico Grape & pomelo
1	7.397	1R-α-Pinene	0.561	0.53	1.10
2	9.154	β-Terpeinene	0.149	< 0.01	nd
3	9.238	Cyclohexene	0.343	nd	nd
4	10.095	β-Myrcene	1.424	2.08	4.20
5	12.176	Limonene	96.925	92.70	77.00
6	30.936	β -Cubebene	0.598	nd	0.10

nd = not detected

3. Citrus peel waste valorisation methods

Biomass valorisation according to Wu et al. (2016), is the process of giving value to various plants and bio-residues, municipal and animal wastes. Citrus peel waste valorisation for green diesel production first requires the extraction of the citrus peel oil. The various methods are: mechanical cold press (MCPM), hydro-distillation (HDM), steam distillation (SDM), microwave assisted distillation (MADM), solvent extraction (SEM) and supercritical fluid extraction (SFE). Uniqueness of these methods is presented in Table 3.

Table 2: Physicochemical properties of LPO in comparison with other fuels (Ashok et al., 2017)

Property	ASTM method	**Diesel	LPO	**B10	* % Difference of LPO from diesel	* % Difference of LPO from B10
Kinematic viscosity (cSt) at 40 ˚C	D445	3.60	1.05	4.16	70.80↓	74.76↓
Density (kg/m^3) at 15 ˚C	D1298	853.80	843.00	855.00	1.26↓	1.40↓
Flash point (˚C)	D93	93.00	54.00	96.00	41.93↓	43.75↓
Cal. Cetane Index	D976	54.60	15.00	54.40	72.53↓	72.43↓
Calorific Value (MJ/kg)	D420	45.28	41.00	44.72	9.45↓	8.32↓
Carbon (wt. %)		84.10	89.94	82.30	6.94↑	9.28↑
Hydrogen (wt. %)		12.80	9.25	12.50	27.77↓	26.00↓
Oxygen (wt. %)		3.90	0.81	4.30	79.23↓	81.16↓

* Author's analysis.
** Physicochemical properties of Diesel and B10 fuel: (Abdul Aziz et al., 2006).
↓: percentage difference of CPO fuel property lower than that of diesel or B10;
↑: percentage difference of CPO fuel property higher than that of diesel or B10.

Table 3: Citrus peel waste valorisation methods

S/N	Method	Description	Advantage/challenges	Yield (%)	Reference
1	MCPM	Subject peels to mechanical pressure via tapered screw press to release oil at room temperature.	Low cost of production. Low yield. Volatile products retain their aromatic properties. Requires additional centrifugation.	1.5 – 7.5	Teigiserova et al. (2021)
2	HDM	Vaporisation of water containing peels to release the oil as condensate and separated via separating funnel.	Purer product than MCPM. Takes longer time than MCPM.	4 – 9.5	Bousbia et al. (2009)
3	SDM	Heat from steam used to vaporize the oil by thermal agitation from the peel and collected as condensate.	Similar to hydro-distillation but with more yield. Higher steam temperature may decompose volatile fractions.	10	Farhat et al. (2011)
4	MADM	Heating via microwave oven using moisture from the peel to vaporize the and collected as condensate.	Takes shorter time compared to other methods. High temperature may decompose some volatile products.	1 – 10.5	Ferhat et al. (2016)
5	SEM	CPO extraction via the use of bio-solvent in Soxhlet apparatus.	Residue contamination. Takes longer time.	Poor yield compared to SFE.	(Mahato. (2019)
6	SFE	Subject working fluid to condition beyond it critical point.	Shorter extraction time. More complicated system. Challenge with polar molecules.	13-times more than MCPM.	Suetsugu et al, (2013)

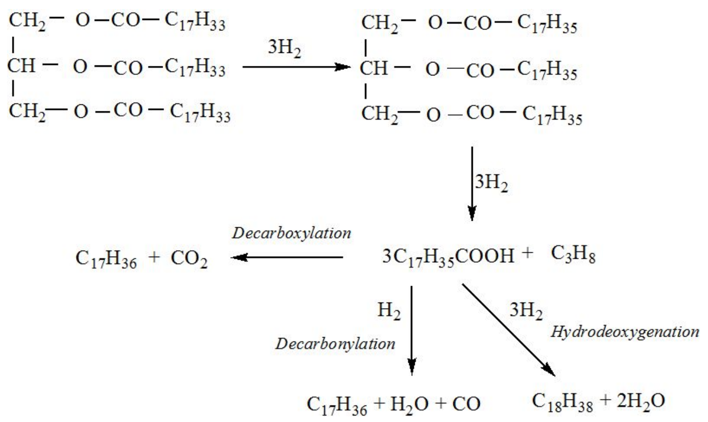
From Table 3 which presents a concise review of the various citrus peel valorisation methods, it could be deducted that MCPM produced oil at relatively low cost, with no oil molecule destruction, however, it suffers low yield and product turbidity as setbacks. While HDM, SDM and MWADM collects the oil as condensate, but higher yield and shorter process time is achieved with MWADM. SEM on the other hand produced oil with improved yield although it suffers residue contamination as setback. SFE though capital intensive and more complicated than the other methods, it is seamless and gives much higher oil yield over a short period of time compare to SEM. Its superiority and uniqueness over SEM, makes it more preferred and suitable for volatile oil extraction e.g., extraction of citrus peel oil. This information is critical to the emergence of a biorefinery producing citrus peel oil for green diesel production and associated value-added products like pectin, biofuel ethanol, biogas, etc.

4. Green diesel production

Green diesel according to Douvartzides et al. (2019) is a new generation biofuel also called “renewable diesel”, “second generation diesel”, “bio-hydrogenated diesel”, “Hydrogenated Esters and Fatty Acids (HEFA)”, “Bio-Hydrogenated Diesel (BHD)”, “Hydrogenation Derived Renewable Diesel (HDRD)”, “Hydro-treated Vegetable Oil” or “Hydrogenated Vegetable Oil” is a mixture of straight chain and branched saturated hydrocarbons which typically contain C_{15} to C_{18}.
Similarly, conventional diesel is a fossil derived fuel composed of a mixture of hydrocarbons with number of carbon atoms ranging from C_{15} to C_{18} in the hydrocarbon chain. It has density, viscosity, flash point and cetane number as shown in Table 2. Biomass derived oils processed to become renewable diesel must assume similar specifications to efficiently burn and develop power in CI engines. Green diesel or renewable diesel is produced from biomass by hydrotreatment of oils or by Fischer-Tropsh process.

4.1 Hydrotreatment of vegetable oils

According to Wang et al. (2018), there are two basic processes involved in the hydrotreatment of vegetable oils to produce green diesel. The breakdown of triglycerides to create fatty acids through hydrogenation is the first step. In the second step, intermediate fatty acids are catalytically deoxygenated to produce hydrocarbons that resemble diesel by three main pathways: decarbonylation, decarboxylation, and hydrodeoxygenation. These processes are illustrated in Eq(1) (Setiawan et al., 2019). The processes take place at elevated temperature over a bifunctional noble or transition metal catalyst.



(1)

4.2 Fischer-Tropsch process

The Fischer-Tropsh process is a catalysed polymerization process in which carbon monoxide and hydrogen called syngas produced via gasification of biomass or coal are converted to short chain and long chain hydrocarbons mainly n-alkanes, olefins and little of alcohol as illustrated in Eqs(2) - (4) (Abatzoglou et al., 2007). Figure 3 depicts the Fischer-Tropsch synthesis (FTS). According to Jenčík (2021), Fischer-Tropsch synthesis is designated the raw material used in the conversion as in gas- to-liquid (GTL) which is when natural gas is used, biomass-to-liquid (BTL) stands for the use of gasified biomass, coal-to-liquid (CTL), when coal dust is used. Low temperature FTS is performed in the temperature range of 200 – 240 ˚C and pressure of 2.5 Mpa over a cobalt (Co) or iron (Fe) catalyst.

$$(2\mathrm{n}+1)\mathrm{H_2} + \mathrm{nCO} \rightarrow \mathrm{C_nH_{2n+2}} + \mathrm{nH_2O} \quad (2)$$

$$2n\mathrm{H_2} + \mathrm{nCO} \rightarrow \mathrm{C_nH_{2n}} + \mathrm{nH_2O} \quad (3)$$

$$2n\mathrm{H_2} + \mathrm{nCO} \rightarrow \mathrm{C_nH_{2n+1}OH} + \mathrm{nH_2O} \quad (4)$$

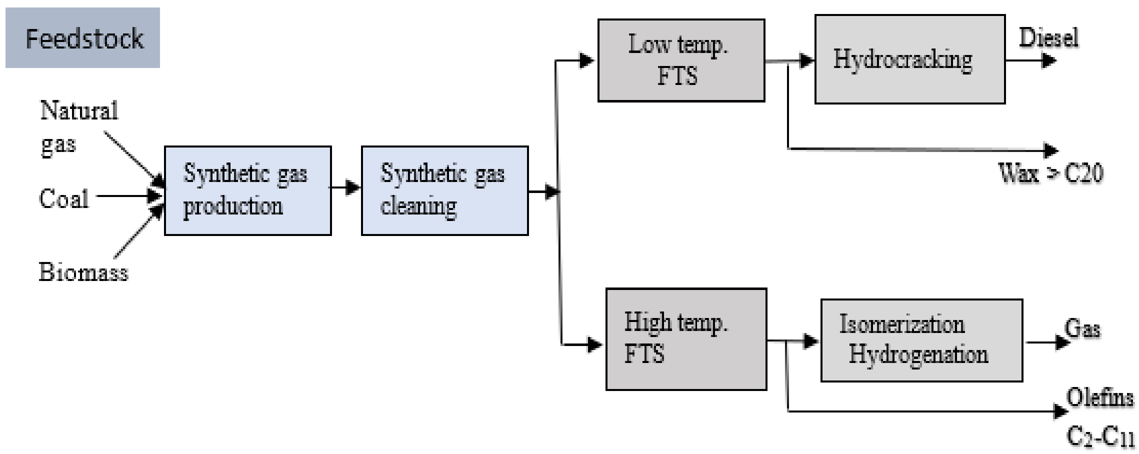


Figure 3: Fischer Tropsch Synthesis for green diesel production (Ltft, 2015)

Even though both Fischer-Tropsch synthesis and catalytic hydrotreatment of vegetable oils produces green diesel, catalytic hydrotreatment is the most suitable and economical method for producing green diesel from citrus peel biomass waste with opportunity for more associated valuable products like pectin, bio-ethanol, biogas, etc, Citrus waste contains about 75 – 85 % moisture (Mahato et al., 2021), hence utilizing fresh citrus peel biomass waste via Fischer-Tropsch will require extensive drying to remove moisture unlike the later. This challenge makes Fischer-Tropsch Synthesis unsuitable compared to hydrotreatment for green diesel production from citrus peel biomass waste.

5. Conclusion

Citrus peel waste valorisation for green diesel production presents a double fold benefit. It contributes in effective waste management of citrus peel biomass waste and provides environment friendly green sustainable energy source in support of the United Nations Sustainable Development Goals number 7 and 13. Citrus peel waste was found to be a very attractive biomass for 2nd generation green diesel production. From the review, Supercritical Fluid Extraction Method was found to be the method with potential for optimal CPO yield even though relatively more complicated than the other methods. Furthermore, physicochemical properties comparison of CPO to a conventional diesel revealed that the percentage difference of density and calorific value of CPO were within the range of the diesel but the percentage difference for flash point, cetane index and kinematic viscosity were significantly out of range of the diesel fuel, a challenge that could be addressed by catalytic hydrotreatment of the oil. The CPO property modification via catalytic hydrotreatment may be the new direction towards a cleaner and greener renewable diesel synthesis.

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References

Abatzoglou N., Dalai A.K., Gitzhofer F., 2007, Green diesel from Fischer–Tropsch synthesis: Challenges and hurdles, Proc. of the 3rd International Conference on Energy, Environment, Ecosystems and Sustainable Development IASME/WSEAS, 24th-26th July, Agios Nikolaos, Greece, 223–232.

Abdul Aziz A., Said M.M.F., Awang M.A., Aziz A.A., 2006, The Effects of Neutralized Palm Oil Methyl Esters (NPOME) on Performance and Emission of a Direct Injection Diesel Engine, Proc. of the 1st International Conference on Natural Resources Engineering and Technology INRET, 24th-25th July, Putrajaya, Malaysia, 646-654.

Alsultan A.G., Asikin Mijan N., Mansir N., Razali S.Z., Yunus R., Taufiq-Yap Y.H., 2021, Combustion and Emission Performance of CO/NOx/SOxfor Green Diesel Blends in a Swirl Burner, ACS Omega, 6(1), 408–415.

Ashok B., Thundil Karuppa Raj R., Nanthagopal K., Krishnan R., Subbarao R., 2017, Lemon peel oil – A novel renewable alternative energy source for diesel engine, Energy Conversion and Management, 139, 110–121.

Balat M., 2006, Fuel characteristics and the use of biodiesel, Energy Sources, 24(9), 855–864.
Bousbia N., Vian M.A., Ferhat M.A., Meklati B.Y., Chemat F., 2009, A new process for extraction of essential oil from Citrus peels: Microwave hydrodiffusion and gravity, Journal of Food Engineering, 90(3), 409–413.
Douvartzides S.L., Charisiou N.D., Papageridis K.N., Goula M.A., 2019, Green diesel: Biomass feedstocks, production technologies, catalytic research, fuel properties and performance in compression ignition internal combustion engines, Energies, 12(5), 809-850.
Farhat A., Fabiano-Tixier A.S., Maataoui M. El, Maingonnat J.F., Romdhane M., Chemat F., 2011, Microwave steam diffusion for extraction of essential oil from orange peel: Kinetic data, extract's global yield and mechanism, Food Chemistry, 125(1), 255–261.
Fatt L., Bokhari A., Asif S., Jaromír J., Joe D., El H., Halim A., Yusof M., 2022, A Review of performance and emission characteristic of engine diesel fuelled by biodiesel, Chemical Engineering Transactions, 94, 1099-1104.
Ferhat M.A., Boukhatem M.N., Meklati B.Y., Chemat F., 2016, Cold pressing, hydrodistillation and microwave dry distillation of citrus essential oil from Algeria: A Comparative Study, Electronic Journal of Biology, S1, 30–41.
Jenčík J., Hönig V., Obergruber M., Hájek J., Vráblík A., Cernˇý R., Schlehöfer D., Herink T., 2021, Advanced biofuels based on Fischer – Tropsch synthesis for applications in diesel engines, Materials, 14, 3077.
John I., Muthukumar K., Arunagiri A., 2017, A review on the potential of citrus waste for D -Limonene, pectin, and bioethanol production A review on the potential of citrus waste for D- Limonene, pectin, and bioethanol production, International Journal of Green Energy, 14(7), 599–612.
Ltft A.T.F., 2015, Recent advances in reactors for low-temperature Fischer-Tropsch synthesis: process intensification perspective, Reviews in Chemical Engineering, 31(3), 209–238.
Mahato N., 2019, Modern extraction and purification techniques for obtaining high purity food-grade bioactive Compounds and Value-Added Co-Products from Citrus Wastes, Foods, 8, 523-604.
Mahato N., Sharma K., Sinha M., Dhyani A., Pathak B., 2021, Biotransformation of Citrus Waste-I: production of biofuel and valuable compounds by fermentation, Processes, 9, 220-269.
Ozturk B., Winterburn J., Gonzalez-Miquel M., 2019, Orange peel waste valorisation through limonene extraction using bio-based solvents. Biochemical Engineering Journal, 151, 107298.
Quyen N.T.C., Ngan T.T.K., Dao T.P., Quynh Anh P.N., Anh N.Q., Nguyen Thi N.T., Ngoc T.T.L., Nhan L.T.H., Truc T.T., Phuong L.T.B., 2019, Essential oil hydrodistillation process from vietnamese calamondin (Citrus microcarpa) peels and GC/MS analysis of essential oils components, Asian Journal of Chemistry, 31(11), 2585-2588.
Setiawan D.I., Irawadi T.T., Alim Z., 2019, Hydrotreating of sunan candlenut (Reutealis trisperma Airy Shaw) oil by using NiMo-γAl_2O_3 as renewable energy, Indonesian Journal of Chemistry, 19(1), 78–88.
Suetsugu T., Tanaka M., Iwai H., Matsubara T., Kawamoto Y., Saito C., Sasaki Y., Hoshino M., Quitain A.T., Sasaki M., Sakamoto J., Goto M., 2013, Supercritical CO_2 extraction of essential oil from Kabosu (Citrus sphaerocarpa Tanaka) peel, Flavour, 2(1), 1–8.
Tan W.T., Jusoh M., Zakaria Z.Y., 2021, Starch-derived solid acid catalyst for biodiesel production: A mini review, Chemical Engineering Transactions, 89, 487–492.
Teigiserova D.A., Tiruta-Barna L., Ahmadi A., Hamelin L., Thomsen M., 2021, A step closer to circular bioeconomy for citrus peel waste: A review of yields and technologies for sustainable management of essential oils, Journal of Environmental Management, 280, 111832.
Wang F., Xu J., Jiang J., Liu P., Li F., Ye J., Zhou M., 2018, Hydrotreatment of vegetable oil for green diesel over activated carbon supported molybdenum carbide catalyst, Fuel, 216, 738–746.
Wu L., Moteki T., Gokhale A.A., Flaherty D.W., Toste F.D., 2016, Production of fuels and chemicals from biomass: Condensation reactions and beyond, Chem, 1(1), 32–58.