Liquid Biofuels Production and Emissions Performance in Gas Turbines: A Review

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Abstract

The increasing demand for clean and sustainable energy sources provides the impetus for the development of alternative fuels. Recent development of fuel-flexible gas turbine technologies enables the use of alternative non-fossil fuels that could play key roles in contributing to the global efforts in meeting emissions targets. This review highlights the current state-of-the-art production and properties of alternative fuels such as straight vegetable oil (SVO), biodiesel, bioethanol, bio-oil, hydrogenated vegetable oil (HVO) and Fischer-Tropsch (FT) fuel. This is followed by the evaluation of combustion performances in gas turbines. All of the alternative liquid biofuels have shown their potentials in reduce regulated emissions such as NO_x, CO and soot under favourable operating conditions. Both HVO and FT fuels show comparable performance as that of jet fuel and can be used in aviation gas turbines, although the present day high production cost restricts the large-scale adoption, limiting its utility. They also have considerably higher cetane number than the rest, making it easier for the fuel to ignite. As for stationary power generation gas turbines that need not carry payloads, the other four alternative biofuels of biodiesel, bioethanol, bio-oil and SVO are possible candidates despite the physics-chemical properties variations when compared to fossil fuels. Amongst them, the use of SVO and bio-oil in gas turbines would require the parallel development of fuel supply systems and atomisation technologies to improve the combustion of the fuels. In all, the alternative liquid fuels reviewed provides realistic opportunities for cleaner and more sustainable operation of aviation and power generation gas turbines. Profound understanding on the fundamental combustion characteristics of the fuels are essential to expedite their mass adoption in gas turbine applications.

Keywords: gas turbine; biofuels; alternative fuel; jet fuel; biodiesel; FT fuel

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1.0 Introduction

Biomass-derived alternative fuels produced from renewable biomass are important owing to them being potentially carbon neutral, producing cleaner combustion and having sustainable feedstock supply from existing plantations [1]. From a carbon cycle perspective, carbon dioxide (CO_2) produced from the combustion of fossil fuels are discharged into atmosphere without recycling, whereas biofuels are potentially carbon neutral as the CO_2 produced from the combustion process is reabsorbed for feedstock plant growth. Fig. 1 compares the CO_2 emission cycle between fossil fuels and biofuels.

At present, the usage of biofuels is not yet prevalent despite the positive benefits to the environment. This is due to the high cost associated with biofuels production and the relatively lower crude oil price in recent years. These form the primary reasons for the continued reliance on fossil fuels for power generation. Fig. 2 shows the price comparison of fossil fuel-based compressed natural gas (CNG) and diesel with biofuels, i.e. biodiesel (B99/B100) and bioethanol (E85) since the turn of the millennium [2]. As expected, fossil diesel is consistently cheaper than biodiesel and bioethanol. CNG is relatively cheaper than all of the liquid fuels compared and hovers around US$2 per gasoline-gallon equivalent (GGE) over the past few years. However, the need for high pressurisation and the low energy density of CNG renders it to be less practical as compared to liquid fuel in terms of storage and the inherent power contained.

The US Energy Information Administration reported that only 10% of total energy produced came from renewable sources in 2016, out of which, about 22% was contributed by biofuels [3]. There have been calls to table climate change policies to limit the consumption of fossil fuels in order to reduce the gap between fossil fuels and alternative energy sources [4,5]. In December 2015, 195 countries agreed to a global climate deal during the UN Climate Change Conference in Paris (COP21) to pledge the reduction of greenhouse gases in order to

achieve a global temperature rise of below 2 °C above pre-industrial levels [6]. Despite the announcement of the US about their withdrawal from the 2015 Paris agreement in June 2017, global efforts on reducing greenhouse gas emissions continue to gain momentum for most countries [7]. One way to achieve the goal of greenhouse gas emissions reduction is by adopting renewable energy sources [6]. The political will and investment committed in sustainable energy technology catalyst have spurred the production of biofuels, which could subsequently lead to reduction of production cost through economies of scale [8].

Gas turbine is one of the power generation systems that contribute to the global greenhouse gases emissions. The technology of gas turbine started exclusively for the aviation industry in the 1960s but rapidly progressed to become an important power generation system. A key milestone that led to gas turbine's rise as a prominent mode of power generation is the development of combined cycle power plants that incorporates the combination of gas and steam turbines, allowing the energy conversion efficiency to be boosted up to around 60% [9,10]. Additionally, most of the combined cycle power plant are fuelled by natural gas, which makes it cleaner than coal-powered power plants [9].

The capacity factor for natural gas powered combined cycle plants between year 2005 and 2015 in the U.S is shown in Fig. 3. The capacity factor increased from an average of 35% in 2005 to 56% in 2015 [11] owing to increasing demand. The increase in usage capacity signifies the inevitable increase of greenhouse gases production, i.e., CO_2. In order to meet the increasingly stringent environmental legislations and emissions targets, recent research has focused on the development of clean, sustainable biofuels and low emission technologies. In the field of gas turbines, fuel-flexibility technology is desirable from the standpoint of meeting emissions goals and reducing operating costs [12,13]. Potential biomass-derived liquid fuels that have been identified as substitute for conventional fuels or supplemental fuels include straight vegetable oil (SVO), biodiesel, hydrogenated vegetable oil (HVO), bioethanol, bio-oil

135 and Fischer-Tropsch (FT) fuel. This paper critically reviews the production process of liquid

136 biofuels, fuel properties and previous studies related to the performance and combustion

137 characteristics under gas turbine operating conditions.

138

139 **2.0   Applications of liquid biofuels in gas turbines**

140 Gas turbine is a power generation system that is known to be fuel-robust and able to

141 accommodate different types of fuels. To substitute fossil-based fuels, biomass-derived

142 alternative fuels are attractive options that have gained much interest in recent years in view of

143 their renewability and potentially lower emissions. The development of different techniques

144 and production processes that convert biomass into bioresource energy in recent decade have

145 been rapid. The production pathways of the main liquid biofuels are shown in Fig. 4. In general,

146 straight vegetable oil (SVO) is produced directly from mechanical, chemical and enzymatic

147 extraction methods. Biodiesel is produced via the process of transesterification of vegetable oil.

148 Hydrogenated vegetable oil is produced from SVO and animal fats that undergo hydrogenation

149 and isomerisation processes. By pyrolysing biomass, bio-oil and synthesis gas can be produced.

150 The synthesis gas that contains H_2 and CO derived from pyrolysis and gasification processes

151 can be used to produce Fischer-Trospch (FT) fuel. Bioethanol is produced from biomass via

152 hydrolysis and fermentation processes. The variety of feedstock and production methods used

153 to produce the biofuels result in significant differences in the physical and chemical properties,

154 which subsequently affects the combustion quality and performance in gas turbines. Thus,

155 understanding the physical, chemical and rheology properties of the fuels is essential to ensure

156 system safety, design of fuel-flexible combustor and optimise the performance of existing gas

157 turbine systems. The following sections review in detail the physio-chemical properties,

158 production methods and combustion performance characteristics of each type of biofuels.

159

2.1 Straight vegetable oil (SVO)

2.1.1 Properties of SVO

Vegetable oil can be used directly as fuel in gas turbines [14,15] and internal combustion engines [16,17]. SVO consists of triglycerides that contain three molecules of fatty acids and one molecule of glycerol [18]. The positive attributes of SVO as alternative fuel are biodegradable, renewable and low sulphur and aromatic content [19]. The viscosity for SVO is about an order of magnitude higher than that of diesel, highlighting the major drawback of SVO in gas turbine application, as shown in Fig. 5. High viscosity of SVO results in inferior atomisation, increases carbon deposition and subsequently reduces combustion efficiency [20,21]. One way to reduce the viscosity of SVO is by preheating the fuel and blend with conventional diesel. Despite the feasible usage of SVO in engines, previous experimental works have shown that the tendency of soot deposition increases with the proportion of SVO in fuel [20,21]. Carbon deposition in the combustion chamber and injection system undesirably shortens the life span of the engine, leading to the increase in maintenance cost [22]. Cetane number is a measure of autoignition quality of a fuel. A fuel that is easier to ignite has higher cetane number. The degree of unsaturation in SVO affects the cetane number. Overall, SVO contains lower cetane number compared to conventional diesel or Jet A-1 as shown in Fig. 5, indicating that SVO is harder to ignite when used as operating fuel. Despite the difference in chemical composition as compared to fossil diesel, the calorific value for SVO (38 MJ/kg) is only marginally lower than that of fossil diesel (42.5 MJ/kg), as indicated in Fig. 5. The calorific value for SVO is lower than fossil diesel by approximately 11% due to the presence of oxygen.

SVO can be derived from a variety of plants such as palm, jatropha, castor, jojoba, karanja, tobacco, rapeseed, sunflower, soybean, candlenut and chestnut. The oil content for these plants typically range from 20-60 %wt [18]. The physical properties of these feedstocks

185 are shown in Table 1. The SVOs from rapeseed, sunflower, palm, peanut and sesame are

186 slightly more viscous (>35 mm^2/s) compared to jatropha, soybean, safflower, and coconut (<35

187 mm^2/s). Castor SVO has a relatively high viscosity of 250 mm^2/s, which is nearly one order of

188 magnitude higher as compared to other feedstock, making it not ideal for the fuel delivery and

189 injection system. The primary constituents of SVO, fatty acid, can be categorised into saturated

190 and unsaturated types. Saturated-chain fatty acid contains no double bonds between the carbons;

191 while unsaturated chain contains double bonds [23]. The degree of unsaturation is one of the

192 main factors that affect the overall physical properties of SVO [19,24]. In general, higher

193 degree of unsaturation (more double bonds in the chain) leads to lower viscosity of the oil

194 [24,25]. This is due to the existence of double bonds in the fatty acid bending the chains,

195 resulting in the existence in liquid form with lower viscosity [24,25]. On the other hand,

196 feedstocks with lower unsaturation degree, such as those of palm and coconut oil tend to have

197 higher cetane number (40-42) when compared with other feedstock [24]. The variation of

198 SVO's calorific value is correlated to the degree of unsaturation, where feedstock with higher

199 unsaturation degree such as soybean, corn, rapeseed and safflower possess higher calorific

200 value (>39.4 MJ/kg) against those with lower unsaturation degree such as coconut, jatropha

201 and peanut (<38 MJ/kg). SVO with higher degree of unsaturation has higher C/H ratio which

202 results in the elevated calorific values. The density for SVO is generally higher than that of

203 diesel owing to the higher molecular weight of the former. Table 1 shows that SVO density

204 can be correlated to the degree of unsaturation, where SVO with higher unsaturation degree

205 (>1.3) has density below 915 kg/m^3 than those with lower unsaturation degree (<1.3) such as

206 palm and coconut (> 915 kg/m^3).

207

208 **2.1.2   Production of SVO**

7

209   The production process of SVO generally consists of five stages: (i) seed storage, (ii)

210   pre-treatment, (iii) oil extraction, (iv) filtration, and (v) storage [19]. As shown in Fig. 4, the

211   methods used to extract oil from seeds or kernels of plants can be categorised as mechanical,

212   chemical and biological extraction [18]. Under mechanical extraction, pressers are used to

213   extract oil. The pressers can be of ram or screw type. Screw presser is able to extract up to 95%

214   of oil from feedstock, while ram presser can extract about 65% of oil from feedstock [18,38].

215   Chemical extraction utilises solvents such as *n-hexane,* bioethanol or isopropyl alcohol for oil

216   extraction [38]. The overall efficiency of the process is governed by the types of solvent used,

217   pH level, particle size, agitation process and operating temperature [18,38]. A major

218   disadvantage of chemical extraction is the generation of hazardous waste water that is

219   detrimental to the environment and human health if left untreated [18,38]. For biological

220   extraction, enzyme such as alkaline protease is used to extract oil from crushed seed. This

221   method is environmental friendly, but the downside is long processing time (6 hours) and low

222   yield (38%) [18]. Post-extraction treatment is needed for all extraction method as the extracted

223   oil typically contains contaminants and is sticky. Filtration and purification processes are

224   applied to remove solid impurities, degum the sticky oil and neutralise the oil by adding alkali

225   such as sodium hydroxide [19].

226

2.1.3   Performance of SVO in gas turbines

228   Direct application of SVO in gas turbine is an attractive option as low cost is incurred

229   from oil processing. However, the viscosity of SVO is an order of magnitude higher than

230   conventional fossil diesel, posing a technical challenge when applied in gas turbine system as

231   highly viscous oil will negatively impact fuel flow delivery and result in inferior spray

232   atomisation process. Some practical steps have been undertaken to overcome the physical

233   properties challenge, including modifying the fuel delivery system by adding fuel preheating

234   capability and using twin-fluid injector that allows variation of the controlling parameters.

235   Blending SVO with conventional fuel is another strategy to maintain low viscosity of the

236   blended fuel. The performances of SVO as a viable gas turbine fuel have been tested by

237   different groups, as shown in Table 2 where the feedstock and control parameters are

238   summarised.

239   Varying the atomising air-to-liquid ratio (ALR) in a twin-fluid atomiser is an effective

240   control parameter to atomise SVO. Niguse and Agrawal [39] reported a reduction of NO_x level

241   by a factor of 4 when the ALR was increased from 2.0 to 3.0 in a swirl burner operated with

242   SVO, but the CO emission was not obvious when compared with baseline diesel. In a lab-scale

243   lean premixing and prevaporising (LPP) burner, Kun-Balog and Sztanko [40] reported a

244   reduction of CO and UHC emissions by more than 50% when atomising rapeseed oil at higher

245   atomising air pressure. Jozsa and Kun-Balog [41] further identified that SVO has poorer

246   stability limit than diesel under LPP burning conditions, particularly at low atomising air

247   pressure. Further increase of atomising air pressure led to increased flame stability with lower

248   CO, while the NO_x emissions for rapeseed oil were found to be lower as compared to baseline

249   diesel. Hashimoto et al. [42] utilised a gas turbine burner with twin-fluid atomiser to examine

250   the combustion characteristics of jatropha oil. Result showed that NO_x emissions for both diesel

251   and jatropha oil were around 50 ppm and decreased monotonically with the increase of air flow

252   rate.

253   The increase of ALR led to higher air momentum to effectively disintegrate the viscous

254   fuel into fine droplets for vaporisation. If insufficient atomising air was imparted, inferior

255   atomisation of SVO causes large droplets to move towards the combustor wall, causing lower

256   burning temperature and incomplete combustion that subsequently leads to higher CO

257   emissions. The SVO spray flame appearances varied with ALRs. At ALR < 2, yellow sooty

258   spray flame was established, indicating a poor fuel-air mixing with high level of soot

259 production. Increasing the ALR to beyond 2 resulted in an improved mixing of fine droplets

260 and air, creating flames that were bluish and analogous to a well-premixed flame [39].

261 As fuel viscosity is inversely proportionate with temperature, preheating the SVO is an

262 effective method to reduce the viscosity to the level of conventional fossil fuel. Sallevelt et al.

263 [43] raised the fuel injection temperature in a series of MGT tests. The SVO's viscosity was

264 reduced significantly by a factor of 3, leading to improved combustion efficiency with 28% of

265 lower carbon monoxide (CO) emissions. Likewise. Chiaramonti et al. [44] managed to achieve

266 CO reduction by 40% relative to biodiesel when combusting preheated rapeseed SVO (120 °C)

267 in an MGT (Garrett GTP 30-67) [44]. Prussi et al. [14] reported that the effect of preheating of

268 SVO on emissions was significant, where CO was seen to reduce by 28% in an 18 kW micro

269 gas turbine when preheating SVO to 120 °C. Preheating the SVO enables direct application in

270 gas turbine with positive effects on emissions.

271 There were some attempts to blend SVO in small quantity with fossil fuel, thus

272 removing the need of preheating. Panchasara et al. [45] tested the blends of 10-30% vol.

273 soybean oil with diesel using a gas turbine type burner. The CO emissions for the SVO/diesel

274 blends were reported to increase by 15% as compared to baseline diesel fuel under constant

275 fuel flow rate. The effects of using different SVO feedstock blends on the emissions were

276 studied by Chiariello et al. [15] in a micro gas turbine system. Two types of oils were used,

277 namely sunflower and rapeseed, under partial and full load micro gas turbine conditions. Result

278 showed that sunflower oil exhibited higher propensity of soot formation compared to rapeseed

279 oil blend by a factor of 16.7, owing to the high content of linoleic acid in the former that

280 promotes for the formation of ethene and ethyne during thermal decomposition which are

281 known to be soot precursor [46]. These results show that SVO blends lower soot emissions,

282 although CO was seen to increase. The inherent difference in SVO composition depending on

283 feedstock is another factor that affects emissions.

284   Despite the high CO emissions, the wide availability, ease of storage, near zero toxicity

285   makes SVO an attractive fuel for micro gas turbines. The issue of high viscosity can be

286   overcome by utilising a twin-fluid atomiser with high ALR and preheating the SVO. Moreover,

287   recent study has shown that using superheated steam as atomising fluid is another possible

288   method of reducing the CO, NO and UHC [40]. These strategies show that SVO can be a

289   potential fuel for micro gas turbine, provided modification to the fuel delivery system and

290   injector system is made to accommodate the high viscosity, and the controlling parameter is

291   optimised to achieve low emissions.

292

293   **2.2   Biodiesel**

294   **2.2.1   Properties of biodiesel**

295   The use of SVO in gas turbine has been associated with many problems, mainly

296   attributed to its high viscosity, low volatility and low cetane number. The SVO can further be

297   processed into biodiesel with properties that meet the European Union and U.S standards.

298   Biodiesel is oxygenated, renewable, biodegradable and inherently contains low level of sulphur

299   [47]. Regardless of feedstock, sulphur content in all biodiesel is below 0.01 %wt, which is

300   lower than standards set by European Union (max 0.02 %wt) and U.S. ASTM (max 0.05 %wt),

301   as shown in Table 3. However, the high viscosity of castor biodiesel does not conform to both

302   EU and US standards. The physical properties of biodiesel are similar to that of diesel in terms

303   of calorific value, viscosity, cetane number and density as shown in Fig. 5. Biodiesel can be

304   used as fuel directly or blended with fossil diesel in engines [48,49]. Table 3 compares the

305   properties of biodiesel from different feedstock against standards.

306   The properties of biodiesel is influenced by the degree of unsaturation of the molecules

307   [24,51]. Table 3 shows that feedstock with low degree of unsaturation (0.62-1.15) such as palm

308   oil and jatropha produce biodiesel with poorer cold flow properties (pour point $\geq$ 0 ℃).

11

309 Although better cold flow properties were obtained for biodiesels with higher degree of

310 unsaturation (> 1.3) such as rapeseed, soybean, and sunflower, they are still considered inferior

311 when compared with diesel (-21 ℃) or Jet A-1 (-47 ℃). Additives are usually added to

312 biodiesel to further improve the cold flow properties. The EU and US ASTM standards require

313 the flash point for biodiesel to be higher than 120 ℃ and 93 ℃, respectively. When compared

314 with conventional fossil fuels, the flash point for typical biodiesel (145 ℃) is much higher than

315 Jet A-l (38 ℃) and fossil diesel (76 ℃), as shown in Fig. 5. The benefit of higher flash point is

316 that storage and transportation of biodiesel becomes relatively safer.

317 Another important property is oxidative stability, which is the measure of reaction rate

318 between the fuel and oxygen. The unstable fuel reacts with oxygen to form gums, sediments

319 and other deposits which subsequently increase the viscosity of the fuel [24]. Table 3 shows

320 that only coconut, palm, rapeseed, canola and castor-based biodiesels fulfil the requirements

321 set by the EU standard (min 6 hours). Sunflower and peanut-based biodiesels are not able to

322 meet the requirement set by US ASTM standard, which is minimum 3 hours. High oxidative

323 stability indicates low degradability tendency and prolongs storage time for biodiesel. The

324 typical storage time for biodiesel is usually not more than six months [52], while diesel can be

325 stored up to 12 months at ambient temperature [53]. Biodiesel has gained much attention as

326 supplemental fuel in recent years. The US has implemented the biodiesel mixture excise tax

327 credit as part of the policy in diversifying energy portfolio [54]. The Malaysian government

328 has implemented mandatory blending of palm-based biodiesel with diesel at B7 for transport

329 and industrial sectors [55] .

330

331 **2.2.2 Production of biodiesel**

332 Transesterification is the most common process used to produce biodiesel. The process

333 converts triglycerides into glycerol and biodiesel in the presence of alcohol and catalyst at

elevated temperature, as shown in Fig. 6. The conversion process is a stepwise and reversible process where alcohol initially reacts with triacylglycerols to produce diacylglycerols and fatty acid alkyl esters. Further reaction leads to the formation of monoacylglycerols and lastly biodiesel and glycerol. The process is reversible, but the reversible rate is usually negligible due to glycerol being not miscible with fatty acid alkyl esters [56]. The catalysts can be of acid, alkaline or enzyme types, depending on the content of free fatty acid (FFA) in the feedstock [57].

In acid catalysed transesterification, hydrochloric acid or sulfuric acid are commonly used [58,59]. Acid catalysts were reported to give high yields (90%) in a relatively short period of reaction time (1 to 6 hours). Meanwhile, acid catalysts can tolerate higher level of free fatty acids compared to alkaline catalysts [47,60]. Apart from acid catalyst, alkaline such as alkaline metal alkoxides and hydroxides, potassium carbonates and potassium hydroxide can also be used as catalyst in transesterification process. Alkaline metal alkoxides was reported to produce even higher yield (96%) of biodiesel in a short period of reaction time (1 to 6 hours) [57]. The use of alkaline, however, is susceptible to the level of free fatty acids. The fatty acid could react with alkaline catalyst to produce soap that inhibits the separation process [61]. Enzymatic catalyst such as lipase was introduced to overcome the complex processing needed for the by-product treatment in acid and alkali catalyst transesterification process [61]. However, low yield (62% to 71%) and long reaction time (up to 8 hours) for this biodiesel production technique is not favoured for mass production [62]. Another technique for biodiesel production without requiring catalyst is by using methanol under supercritical condition [63]. This supercritical process requires severe operating conditions such as temperature greater than 240 °C and pressure greater than 80 bar [64]. As catalyst is not used in this process, the by-product treatment process is simpler due to the absence of contaminants. The advantage of this process is short reaction time compared to catalytic-based process [63], but the disadvantages

359   are requirement of expensive equipment and high production cost [1]. Methods of producing

360   biodiesels from various types of lipids are summarised in Fig. 4.

361

362   **2.2.3**   **Performance of biodiesel in gas turbines**

363   Biodiesel has proven to be a viable substitute fuel or as blend with diesel in

364   compression-ignition engines due to its close resemblance to diesel in physical properties [65].

365   Further applications of biodiesel in gas turbines system for power generation and as aviation

366   fuel are envisaged. Land-based industrial gas turbine is fuel-robust in nature that allows the use

367   of biodiesel with minimal modification to the existing system but application in aviation-based

368   gas turbine requires stringent compliance to the jet fuel specification. Table 4 and 5 summarise

369   the previous combustion research related to biodiesel combustion in gas turbine type burners

370   and system. It is noted that biodiesels produced from different types of feedstock have been

371   used for testings.

372

373   *2.2.3.1. Biodiesel spray flame characterisation using gas turbine type burner*

374   The potentials of biodiesel as gas turbine fuels have been investigated using lab scale

375   gas turbine type swirl flame burner. The advantage of using simplified burner allows

376   parametric studies, including comparison of combustion performances, flame structure,

377   emissions with baseline fuels under well-controlled environment. Chong and Hochgreb [66]

378   compared the combustion characteristics of palm [28] and rapeseed [67] biodiesels with

379   baseline diesel and Jet-A1. Biodiesel flames exhibited larger heat release area compared to that

380   of baselines [68]. Soot was not present in biodiesel flame owing to the absence of aromatic

381   rings in the fuel and the fuel-bound oxygen content that assist in the oxidation of soot during

382   combustion. The NO emissions were shown to reduce by ~25% for palm biodiesel as compared

383   to Jet A-1 and diesel at fixed power output of 6 kW [28].

Other researchers who have found the benefits of reduced emissions for biodiesel under swirl flame conditions including Hashimoto et al. [42]. The smoke and soot emissions of jatropha/diesel blends were significantly lower than that of diesel, resulting in lower flame radiation intensity for the biodiesel blends flames. They demonstrated in a gas turbine burner equipped with a pressure atomiser that NO_x emissions for palm biodiesel can be lowered by generating finer spray droplets via increasing the atomising pressure. Finer droplets evaporated at a shorter time scale, reducing localised hot regions that promotes NO_x formation due to droplet burning in diffusion mode [69,70]. Erazo et al. [71] showed that the peak temperature of canola biodiesel (1750 K) was lower compared to diesel (1900 K), hence lower NO_x emissions were detected for the former. Li et al. [72] utilised a gas turbine type burner to compare the spray and combustion properties of rapeseed biodiesel with diesel. Biodiesel spray was found to exhibit longer spray penetration length and smaller spray cone angle compared to diesel owing to its higher density, viscosity, surface tension and boiling point. Similar to the findings shown by Chong and Hochgreb [73], rapeseed biodiesel produced lower NO_x emissions by 21% compared to diesel.

Panchasara et al. [45] noted that inferior atomisation for biodiesel is the main factor that promotes NO_x formation. Adjusting the control parameter presents an effective way to improve emissions. Sequera et al. [74] atomised biodiesel using an airblast atomiser and reported a reduction of CO emissions by 50% for biodiesel as compared to diesel under constant fuel mass flow rates. Chong and Hochgreb [68,73] utilised a twin-fluid atomiser and showed that the twin emissions reduction of NO and CO can be effectively achieved with increasing ALR. Simmons and Agrawal [75] employed a flow blurring atomiser to atomise biodiesel and reported a reduction of CO emissions by a factor of 2-3 when the ALR was increased from 2.0 to 2.4 compared to the typical airblast atomiser. The improved emissions were due to increased mixing from flow blurring. A group of researchers from Cardiff

409 investigated the spray combustion characteristics of biodiesel and biodiesel saturated with

410 pyrolysis oil. The biodiesel/pyrolysis oil blend was found to produce higher NO_x emissions

411 than kerosene, while biodiesel shows comparable NO_x with the latter [76]. Despite no

412 explanations yet can adequately elucidate the biodiesel-NO_x effect based on the previous

413 studies, some recent opinions skewed towards fuel chemistry as the fundamental cause of

414 increased biodiesel NO_x emissions [51,77,78].

415

416 *2.2.3.2. Application of biodiesel in gas turbine system for power generation*

417 The performances of biodiesel combustion at system levels have been tested using

418 actual gas turbines, including those of micro gas turbine, industrial and aviation gas turbine

419 engines. Micro gas turbine can be used for off grid power generation for households, small

420 businesses and rural regions, thus the ability to operate on biodiesel is of interest. Bolszo and

421 McDonell [79] operated a 30 kW MGT (Capstone C30) with soy-based biodiesel and reported

422 higher NO_x emissions than diesel fuel by approximately 13 ppm. Larger droplet size was

423 generated by biodiesel during spray atomisation, leading to higher NO_x emissions as a result

424 of longer evaporation time scale. In another separate MGT (Capstone C30) test, Krishna [80]

425 reported lower NO_x emissions by 60% and 14% for soybean biodiesel at high and low thermal

426 input, respectively, compared to fossil diesel. Both tests showed that soy-based biodiesels could

427 produce conflicting results even in the same gas turbine systems.

428 Nascimento et al. [81,82] compared the thermal performance and emissions of castor

429 biodiesel and blends with diesel in a 30 kW MGT. CO emissions were found to increase by

430 50% as compared to diesel at 14 kW engine output power. It was opined that the lower NO_x

431 emissions achieved in the MGT tests were partly contributed by the inferior atomisation of

432 biodiesel which resulted in lower combustion temperature. The size of biodiesel liquid droplets

433 and primary-zone equivalence ratio were larger for biodiesel compared to diesel. The reduction

16

434   of temperature in primary combustion zone (due to higher equivalence ratio) reduced the

435   emission levels of NO_x pollutants for biodiesel. For MGT that utilises air-blast atomiser, the

436   production of NO_x is affected by the variation of atomising air to liquid ratio. The increase in

437   the percentage of atomising air results in leaner combustion and lower flame temperature,

438   hence the lower NO_x emissions [68,74].

439   Habib et al. [83] utilised a 30 kW gas turbine engine to examine the performance of

440   soy, canola, recycled rapeseed biodiesel and hog-fat biofuel against Jet A. NO emissions for

441   biodiesel were consistently lower than diesel at lean-burning conditions, with a maximum

442   reduction of up to 75%, while the difference in turbine inlet and exhaust gas temperature

443   between biodiesel and diesel was less than 80 °C and 20 °C respectively. CO emissions were

444   found to be lower for biodiesels as the oxygen in the biodiesel assisted in converting CO into

445   CO_2 [83,84]. The static thrust produced by biodiesel and blends were comparable to that of jet

446   fuel. They reported that fuel efficiency was higher when operating with biodiesels, owing to

447   the oxygen in biodiesel that resulted in more complete combustion [83]. Some have reported

448   improved gas turbine performance due to the oxygen content in biodiesel [81].

449   The notion of fuel-flexible industrial gas turbine operation is attractive from the point

450   of view of lower operating cost and adaptability to local biofuel sources. Several gas turbine

451   tests have been conducted using biodiesels. Liu et al. [85] investigated the ignition, combustion

452   dynamics and emissions of biodiesel using a Siemens SGT-100 gas turbine. The NO_x emissions

453   for biodiesel were found to be lower than that of diesel for all operating conditions tested. In a

454   semi-closed cycle gas turbine field test conducted by Ellis et al. [86], soot emissions were

455   shown to reduce by 70% and 32% for palm and soy biodiesels, respectively. No significant

456   trend was observed for UHC emissions for all fuels tested despite slightly higher fuel

457   consumption rate for pure biodiesel by 4-7%. Moliere et al. [87] tested rapeseed biodiesel in a

458   GE 6531B industrial gas turbine. No visible smoke was observed during biodiesel combustion

459 and sulphur oxide emissions were less than 1 ppm. These results indicate the positive effects

460 of biodiesel towards the environment. However, there was a reported case where higher UHC

461 emissions were observed when blends of biodiesel (fish oil and canola oil based) with Jet A1

462 fuel were used in an industrial gas turbine sector rig (Allison/Rolls Royce T56-A-15

463 combustion systems), accompanied by a slight increase in engine deposits for 20% biodiesel

464 blends due to excessive gum and inferior atomisation [88]. These studies show that due to

465 complexities of gas turbine operation, extensive testings are required when using alternative

466 fuels, as the effect of fuel is not restricted to only combustion, but also downstream of

467 combustor such as the turbine blades.

468   Power generation for aviation gas turbine is another area that is extensively explored in

469 search for cleaner alternative fuels to replace fossil-based fuels. Although biodiesel is

470 oxygenated, slightly denser and contains lower heating value than conventional jet kerosene,

471 blending biodiesel with jet fuel could result in positive emission benefits without incurring

472 significant performance penalty. Timko et al. [89] achieved lower NO_x by 29% and 23% for

473 40% and 20% biodiesel blends, respectively in an aviation gas turbine engine (CFM56-7B

474 turbo-fan engine) test. In another biodiesel test in a helicopter turboshaft engine (T63-A-700),

475 Corporan et al. [90] reported that 20% soybean biodiesel/JP-8 blend produced 15% reduction

476 in particle number density at cruising and take-off conditions. Rehman et al. [84] concluded

477 that the oxygen content in a jatropha/diesel blends assisted in the combustion of a 44 kW gas

478 turbines (IS/60 Rovers). Biodiesel was shown to have better fuel efficiency than diesel despite

479 a slight reduction in brake specific fuel consumption (BSFC) by 0.5 kg/kW-hr. The blends

480 however, showed higher emissions of NO_x by 34-42% compared to diesel at the same power

481 output. It was postulated that the higher oxygen content in biodiesel led to higher flame

482 temperature and subsequently higher level of NO_x emissions. Talib et al. [91] utilised a turbojet

483 engine (Armfield CM4) to test the performance of 20% biodiesel/diesel blend compared to Jet

484 A-1 baseline. It was reported that the former fuel produced a lower thrust by 4%, as expected

485 as the energy content of biodiesel is lower than jet fuel by approximately 17% by mass [28].

486 These results showed that application of biodiesel in aviation gas turbine is feasible with the

487 benefits of lower emissions but at the expense of performance penalty.

488

489 **2.3   Hydrogenated vegetable oil (HVO)**

490 **2.3.1   Properties of HVO**

491   Hydrogenated vegetable oil (HVO) is also known as green diesel, renewable synthetic

492 diesel, hydrogenated straight vegetable oil (HSVO), hydrodiesel or hydrogenation-derived

493 renewable diesel (HDRD) [92]. Similar to SVO and biodiesel, plants such as rapeseed, palm,

494 castor, sunflower, jatropha, soybean, and animal fat have been used as feedstock to produce

495 HVO [93,94]. The advantage of HVO is its compatibility with existing diesel engine [26,95]

496 and with nearly 0% oxygen content [93,96]. The biodegradability of HVO is poorer compared

497 to SVO and biodiesel [92–94,96].

498   The calorific value for HVO is higher than that of biodiesel by 16% per mass basis and

499 is comparable with fossil diesel and Jet A-1, as shown in Fig. 5. The cetane number for HVO

500 is higher than both biodiesel and diesel, indicating reduced ignition delay time for engine. The

501 density for HVO is similar to Jet A-1, but less dense than biodiesel and diesel, which makes

502 HVO a good substitute for conventional fuels without incurring weight penalty. The low

503 freezing point of HVO (-25 ℃ to -40 ℃) fulfils the requirement of jet fuel to avoid formation

504 of wax in the fuel supply system. Furthermore, HVO has comparable viscosity as Jet A-1 and

505 diesel. The comparable physical properties of HVO with Jet fuel has enabled the former to be

506 certified as alternative jet fuel [4].

507

508 **2.3.2   Production of HVO**

19

509   HVO is produced via hydrogenation of vegetable oil in the presence of catalyst and

510   hydrogen [26,95]. The process breaks the double bond (C=C) in the vegetable oil into single

511   bond (C-C). Hydrogen was inserted into the hydrocarbon chain. Apart from carbon and

512   hydrogen atoms, other elements such as sulphur, nitrogen, and oxygen are present in HVO [96].

513   The presence of these heteroatoms is highly undesirable; as oxygen tends to reduce the heating

514   value while sulphur promotes the formation of sulphur dioxide during combustion process.

515   Hydrogenation process removes these heteroatoms to improve the overall quality of the fuel

516   [26,95]. The hydrogenation process mainly consists of two steps: hydrotreatment that saturates

517   the unsaturated fat (i.e. breaking the C=C), and isomerisation process that forms the branched

518   chains [26,95].

519   The research on hydrotreatment of vegetable oils has mostly focused on the type of

520   reactors and catalysts. Two types of catalysts were reported to be effective in hydrotreatment

521   of vegetable oils process, namely metal catalysts and sulfided bimetal catalysts [94]. The

522   overall process of hydrogenation of vegetable oil is shown in Fig. 7. Feedstock is supplied to

523   the catalytic reactor to combine with hydrogen at elevated temperature and pressure. The

524   feedstock is pretreated prior sending into reactor. In the reactor, the feedstock undergoes the

525   hydrodeoxygenation, decarboxylation, and hydroisomerisation processes to convert into diesel,

526   water, and oxide of carbon [92]. The hydrotreatment process takes place in a fixed bed reactor

527   at elevated temperature of 300-400 °C and pressure of 30-130 bar in the presence of catalyst.

528   The HVO yield varies from 88% to 99%, depending on the type of feedstock [92]. The

529   produced diesel fuel contains no sulphur, oxygen, aromatic and nitrogen.

530   **2.3.3 Performance of HVO in gas turbines**

531   HVO has been identified as a promising alternative jet fuel due to the absence of oxygen

532   molecules and comparable physical properties to jet fuel [4]. A study conducted by Chan et al.

533   [97] using a turbofan engine (CF700-2D-2) fuelled with HVO has shown lower NO_x emissions

compared to Jet A-1. At idling conditions of 80% and 95% engine loads, the 50% HVO/Jet A-1 blend produced up to 0.3 g/kg lesser NO_x than neat Jet A-1. The result concurs with Baranski et al. [98] in a turbojet engine (JetCat P-200) test fuelled with HVO and JP-8, where NO_x emissions for HVO were shown to be consistently lower than that of JP-8 at all operating speeds. The thrust specific fuel consumption for HVO was 16% lower than that of JP-8 at engine speed below 60,000 rpm.

Klingshirn et al. [99] reported lower CO emissions in a gas turbine (T63 A-700) test fuelled with HVO compared to baseline JP-8. CO emissions were consistently lower than that of JP-8 at both the idling and cruising modes with fuel/air ratios of 0.009 and 0.017, respectively. The effect of altitude on the emissions of CO by hydrogenated fuel was investigated by Chishty et al. [100]. The gas turbine performance test was conducted at the altitudes of 1525 m and 6095 m with Jet A-1 and blend of 50% JP-8/hydrogenated renewable jet fuel. Jet A-1 showed higher CO emissions as compared to the blend. The exhaust CO was around 175 g/kg fuel at 6095 m, which is significantly higher than at 1525 m which was about 125 g/kg fuel. Jet A-1 showed slightly higher NO_x emissions than JP-8/hydrogenated fuel blend by a slight difference of 0.3 g/kg fuel.

The improved emission performance of HVO was also reported by Purcher et al. [88,101] in a gas turbine (Allison/Rolls Royce T56-A-15) test operated with HVO. The particulate matter and unburned hydrocarbon emissions were reduced by 96% and 27.7% respectively as compared to baseline Jet A-1. HVO has shown overall positive emissions as opposed to that of fossil jet fuel. Soot concentration and mass deposition were found to reduce significantly for HVO. On top of that, the ignition delay time is also shorter and resistance to extinction is stronger compared to Jet A [102]. Buffi et al. [103] investigated the heat release and emissions profiles of Jet A-1, HRJ (Hydrotreated Renewable Jet Fuel) and their blends using an optical swirl burner. It was reported that HRJ exhibited a more homogenous heat

559 release zone that led to reduced emissions. Meanwhile, the effect of backpressure was also

560 examined, whereas the reduced bulk flow was due to the increase of backpressure that formed

561 a more compact flame brush.

562

563 **2.4 Bioethanol**

564 **2.4.1 Properties of bioethanol**

565 Bioethanol is a colourless, biodegradable, low toxicity, and highly flammable liquid.

566 Bioethanol has relatively low viscosity (1.5 mm^2/s) and pour point (-78 ℃) which are

567 comparable to jet fuel, as shown in Fig. 5. However, the downside of bioethanol is its low

568 calorific value (only around 63% of fossil diesel) and low flash point (14 ℃). In addition, the

569 low flash point characteristic makes bioethanol an explosive hazard [104].

570

571 **2.4.2 Production of bioethanol**

572 Bioethanol is produced by fermentation of sugar units derived from the sugar-

573 (sugarcane, sugar beet), starch- (corn, wheat, barley) or cellulosic- (rice straw, wheat straw,

574 wood) based biomass [105]. The pure sugar biomass feedstock (sugarcane and sugar beet) is

575 relatively straightforward to be converted into bioethanol, due to fermentable sugar units that

576 can be obtained relatively easy during extraction process of raw material. Starch-based

577 feedstock such as corn and wheat are more complicated due to the long chain polymers of

578 glucose that cannot be directly fermented. The polymers have to be broken down into

579 monomers before fermentation process [106–108]. Cellulosic feedstock such as wood, straw

580 and bagasse are the most difficult feedstock to breakdown as compared to sugar and starchy

581 biomass due to their constituent parts [106–108].

582 The production process of bioethanol consists of (i) pre-treatment, (ii) hydrolysis, (iii)

583 fermentation and (iv) purification processes [106–110], as shown in Fig. 4. The purpose of pre-

584 treatment is to break the lignin and cellulose structure of the feedstock to make the feedstock

585 more susceptible to enzymatic attack in hydrolysis process. Sugar biomasses such as sugarcane

586 and sugar sorghum are usually mechanically crushed to extract the sugary juice from their

587 stalks. For starchy-based feedstock, the dry or wet milling processes are commonly used [106–

588 109]. Lignin provides the rigid structure for cellulosic feedstock. Thus, the conversion of

589 lignocellulosic feedstock into ethanol is more difficult compared to sugar and starch based

590 feedstock [106–108]. Steam explosion is one of the pre-treatment methods for cellulosic

591 feedstock, whereas the feedstock is exposed to high pressure saturated steam to break the lignin

592 structure so that the feedstock is more susceptible to hydrolysis [106,110].

593 Following the pre-treatment is the hydrolysis process which degrades the cellulose and

594 hemicellulose from the raw material into simple sugar units for the fermentation process.

595 Enzymatic hydrolysis has the advantage over the chemical hydrolysis for its lower cost [105].

596 Cellulase enzymes are typically used to convert the complex cellulose and hemicellulose into

597 simple monomers [111–113]. Fermentation is the process in which sugar units are converted

598 into bioethanol due to the enzymes secreted by microorganisms. Baker's yeast (Saccharomyces)

599 is usually used to convert the glucose into ethanol [105]. Factors that affect the efficiency of

600 fermentation are pH range, genetic stability, temperature range, inhibitor tolerance, and alcohol

601 tolerance [105]. More complex sugar unit such as pentose and hexoses are usually more

602 difficult to be fermented compared to glucose. Nonetheless, several methods have been

603 introduced for pentose and hexoses fermentation, these include using genetically modified

604 microbes [108,114], combination of both fermentation and enzyme hydrolysis [115], mixed

605 cultures of yeasts [116] and fermentation of the pentose and hexose sugars simultaneously in a

606 single reactor by a single microorganism's community [108,109,117].

607

608 **2.4.3   Performance of bioethanol in gas turbines**

609   Bioethanol is commonly utilised as replacement for gasoline to power the internal

610   combustion engine. One of the commonly used bioethanol blends is E85, which contains 85%

611   bioethanol/ethanol and 15% gasoline. Ethanol-gasoline blends with minimum 10% ethanol

612   proportion are known as gasohol. Gasohol is common in countries such as Brazil, Denmark

613   and the US [118]. Sallevelt et al. [119] examined the emissions of bioethanol combustion in a

614   gas turbine engine (OPRA 2MWe OP16). NO_x emissions for bioethanol were 50% lower than

615   that of diesel for equivalence ratios between 0.15 - 0.35 due to lower thermal NO_x. Moliere et

616   al. [120] reported that neat bioethanol emits 50% NO_x lower as compared to neat naphtha in

617   an industrial gas turbine (GE Frame 6B). Despite lower emissions of NO_x for bioethanol, CO

618   emissions were rather inconsistent [119–121]. Santos and Nascimento [122] fuelled a 30 kW

619   gas turbine with bioethanol at different loadings. A slight increase in CO was observed.

620   Meanwhile, Khalil and Gupta [121] examined the combustion and emissions performance of

621   bioethanol using a swirl burner. Fuel and preheated air were premixed upstream of the

622   combustor prior to injection into the combustion chamber at high velocity (96 m/s) tangentially

623   and in swirling mode. Bioethanol was shown to produce lower CO emissions as compared to

624   kerosene under lean burning mode. Maximum reduction of was up to around 40 ppm at

625   equivalence ratio of 0.8. The decrease in CO emissions was attributed to the excess oxygen

626   that converts CO to CO_2.

627   Breaux and Acharya [123] studied the effect of water content in ethanol combustion

628   using a swirl burner. It was found the water content reduced the flame temperature. When water

629   content is below 20%, the effect of water on combustion performance was only minor and

630   regarded as insignificant. However, as the water content increased beyond 20%, it impaired the

631   continuous combustion process. Due to reduced flame temperature, NO_x emissions were found

632   decreased from 13 ppm to 3 ppm for 0% and 30% of water content, respectively. Kun-Balog

633   et al. [124] experimentally investigated the emission characteristics of bioethanol in both liquid

634 and aqueous form against diesel and natural gas (NG). The experiment was conducted using a

635 lab-scale swirl burner. The use of bioethanol resulted in 44% lower NO_x than diesel under the

636 same thermal power output, which was attributable to the lower adiabatic flame temperature.

637 The CO and UHC emissions were relatively low for bioethanol. However, aqueous bioethanol

638 resulted in higher NO_x than its liquid counterpart.

639

640 **2.5   Bio-oil**

641 **2.5.1   Properties of bio-oil**

642 Bio-oil is liquid fuel obtained from the biomass pyrolysis. Bio-oil is also known as

643 pyrolysis oil or bio-crude [125]. It is usually dark brown in colour and consists of organic

644 compounds mixture. The pyrolysis process for the production of bio-oil involves heating of

645 organic compound such as cellulose, hemicellulose and lignin in the absence of oxygen [125].

646 The process produces a range of products including char, bio-oil, and gaseous products. The

647 composition of bio-oil depends on the temperature of the pyrolysis process [105]. At pyrolysis

648 temperature below 600 K, formation of char is dominant. At temperature beyond 800 K,

649 gaseous formation is dominant due to increased reaction rates that break the bond between

650 carbons. For temperature in between 600 K and 800 K, bio-oil formation is dominant [105].

651 Table 6 shows the composition of bio-oil derived from several feedstocks [126]. Feedstock

652 with high water content such as barley straw produces bio-oil with lower calorific value.

653 Typical pyrolysis oil produced from feedstock with moderate water content (20-27% wt)

654 contains approximately 15-16 MJ/kg of calorific value. While it was demonstrated that palm

655 oil sludge is a promising feedstock, bio-oil produced from palm oil sludge resulted in notably

656 higher calorific value (22.2 MJ/kg) and lower ash contents (0.23 wt%) [127].

657 Bio-oil is corrosive as it contains substantial amount of formic and acetic acids. Other

658 trace elements such as sodium, calcium, potassium, and vanadium in pyrolysis oil are

659 undesirable as they lead to formation of solid deposition [125,128]. The viscosity of bio-oil is

660 relatively high (15.5 mm^2/s). These undesirable properties of bio-oil have restricted the usage

661 in practical combustion system [129] despite having the advantages of being renewable,

662 sustainable and potentially CO_2 neutral. Post-production methods have been introduced to

663 improve the properties of bio-oil such as (i) hydrodeoxygenation, (ii) hydro-cracking, (iii)

664 emulsification, (iv) steam reforming and (iv) esterification to enable applications in combustion

665 systems [130].

666

2.5.2   Production of bio-oil

668   Bio-oil can be produced by 3 different processes, i.e. (a) conventional pyrolysis; (b)

669 fast and flash pyrolysis and (c) hydrothermal liquefaction (HTL) [105,130], as shown in Fig.

670 4. Conventional pyrolysis operates in the temperature range of 300-650 °C. The residence time

671 is relatively long, typically exceeding half an hour for each batch. Recent studies showed that

672 the yield of bio-oil can be increased with elevated temperature and residence time [131]. The

673 process breaks up the chemical bonds in the feedback, leading to the formation of pyrolysis

674 products [105,130,132]. Fast pyrolysis requires higher operating temperature (650-1000 °C) to

675 decompose the feedstock. The feedstock for pyrolysis can be of any organic biomass. Wood,

676 agricultural wastes, crops, and sewage sludge have been utilised as feedstock for this process

677 [130]. Due to high operating temperature, short residence time of less than 0.2 hour is required.

678 The rapid heating of biomass leads to the formation of volatile vapours, aerosols and char.

679 After rapid cooling, the volatile vapours and aerosol condense into bio-oil [128,133,134].

680   Flash pyrolysis operates at the temperature as high as 1200 °C. This process requires

681 the shortest residence time (< 0.1 hour) as compared to other forms of pyrolysis. A major

682 advantage of flash pyrolysis is the improved overall energy efficiency of the process

683   [105,130,132]. The reactor used for fast and flash pyrolysis has to be able to achieve high

684   heating and heat transfer rate to minimise the formation of char.

685   Hydrothermal liquefaction (HTL) produces bio-oil in an aqueous medium that

686   involves a series of complex processes such as solvolysis, dehydration, decarboxylation, and

687   hydrogenation. The typical operating conditions are temperature ranging 300-400 °C, pressure

688   up to 20 bar, and residence time of 0.2-1 hour. The primary product derived from this process

689   is bio-oil. Contrary to fast and flash pyrolysis, feedstock drying is not necessary, making it

690   suitable for wet biomass [130].

691

692   **2.5.3   Performance of bio-oil in gas turbines**

693   Gas turbine fuelled with bio-oil generally emits lower NO_x emissions as compared to

694   baseline fuels [135,136]. Beran and Axelsson [136] studied the combustion properties of bio-

695   oil using a micro gas turbine (OPRA OP-16). Emission results showed that NO_x emissions of

696   bio-oil was 25% of that emitted by diesel at full engine loading, which is expected considering

697   the lower calorific of bio-oil (37.6%) compared to the latter. Zheng and Kong [137] studied the

698   emissions of rice husk bio-oil using a combustor fitted with an internal-mixed atomiser. Results

699   showed that NO_x concentration increased from 211 to 370 ppm while SO_x concentration

700   increased from 11.6 to 25.9 ppm as equivalence ratio increased from 1.2 to 2.0. The increase

701   of NO_x emissions was due to oxidation of nitrogen in post-flame region and oxidation of

702   nitrogen compounds in the fuels.

703   Lopez Juste and Salva Monfort [138] compared the combustion performance of JP-4

704   and 80% bio-oil/ethanol blends by using a gas turbine burner equipped with pressure swirl

705   atomiser. The emissions of NO_x for bio-oil/ethanol blend were found to be similar to JP-4 at 1

706   MJ/kg energy input. At a higher energy input of 1.36 MJ/kg, NO_x emissions for JP-4 were 4

707   times higher than bio-oil, possibly due to higher flame temperature exhibited by JP-4. Lupadin

708   et al. [135] compared several types of alternative fuels against diesel by using a 2.5 MW gas

709   turbine (GT2500) as shown in Table 7. For bio-oil, higher fuel flow rate was needed to achieve

710   comparable output power and exhaust gas temperature as baseline diesel. The fuel flow rate

711   required by diesel to generate 2510 kW of output power was 1071 l/hr while bio-oil required

712   1800 l/hr of fuel supply to generate 2650 kW of output power. The exhaust gas temperature for

713   both fuels was only differ by 17 °C. Bio-oil emitted higher CO and lower sulphur oxide

714   emissions compared to baseline fuels.

715   Zadmajid et al. [139] reported that bio-oil and 80/20 bio-oil/ethanol blend showed high

716   emissions of CO at 2284 and 650 ppm, respectively, under swirl burning condition. By using

717   a modified burner with increased swirl and main air supply, the CO and UHC emissions

718   showed significant reduction to below 10 ppm. Apart from burner geometry, the choice of

719   feedstock and quality of bio-oil are important factors that determine the level of emissions.

720   Table 6 shows that bio-oil produced from wood contains higher calorific value and lower

721   viscosity than the other feedstock. Although combustion of bio-oil has shown lower sulphur

722   and nitrogen oxide emissions, direct usage of bio-oil in gas turbine are limited due to inherent

723   inferior properties such as high viscosity and acidity level. Direct bio-oil usage caused high

724   level of particulate matter emissions, while other issues related to bio-oil are solid deposition

725   on turbine due to the presence of trace elements and fuel nozzle blockage during operation

726   [140]. The high viscosity of bio-oil affects fuel atomisation which subsequently leads to

727   reduced combustion efficiency. Preheating of fuel and improvement in atomisation technique

728   can be applied to reduce fuel viscosity. Crayford et al. [141] reported that bio-oil exhibited

729   spray characteristics similar with diesel when preheated the fuel to 80 °C.

730   **2.6   Fischer-Tropsch (FT) fuel**

731   **2.6.1   Properties of FT fuel**

732   Fischer-Tropsch (FT) synthesis refers to the process of converting syngas into liquid

733 fuels at high temperature conditions in the presence of catalyst [105,132], as shown in Fig. 4.

734 FT fuels are clean compared to fossil fuels due to the absence of nitrogen, sulphur, and

735 aromatics. Hydrocarbon fuels of different chain length can be produced from FT synthesis via

736 any feedstock that contains carbon, e.g. coal, biomass and natural gas. It has been reported that

737 FT fuel is compatible with existing jet engine systems [105] with calorific value of 43 MJ/kg,

738 viscosity of 1.3 mm^2/s at 40 °C and density of 810 kg/m^3 at 15 °C (Fig. 5). These properties

739 are comparable with Jet A-1, making it a potential alternative jet fuels besides HVO [26,142].
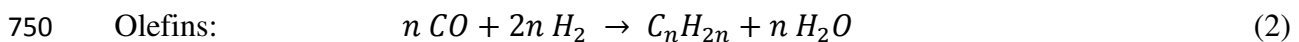
740

741 **2.6.2 Production of FT Fuel**

742   The process of producing FT fuel consists of three main stages as shown in Fig. 8: (i)

743 gasification of biomass into syngas; (ii) gas cleaning and conditioning, and (iii) FT synthesis

744 to produce liquid fuel [105].

745   The FT process is essentially a stepwise hydrocarbon chain growth process that

746 disintegrates the carbon monoxide and hydrogen in the syngas to form mainly paraffins and

747 olefins as shown in reactions 1 and 2 [143]:

748

749 Paraffins: $n\,CO + (2n+1)H_2 \;\rightarrow\; C_nH_{2n+2} + n\,H_2O$ (1)

750 Olefins: $n\,CO + 2n\,H_2 \;\rightarrow\; C_nH_{2n} + n\,H_2O$ (2)
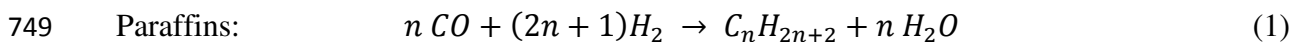
751

752   Both reactors and catalyst are the governing factors that control the products of FT

753 synthesis. Three reactors have been designed and widely used for FT fuel synthesis, namely

754 fixed bed, fluidised bed and slurry reactors [105], as shown in Fig. 9. Fixed bed reactors consist

755 of catalyst tube bundles immersed in steam, whereby the heat from the surrounding steam is

756 absorbed to achieve the FT synthesis process as syngas flows through catalyst tube bundles.

757 Despite easier to operate, the major drawback is its high capital cost and maintenance work

758 that involves high cost and long down time, which impairs the overall efficiency of the plant

759 [144].

760   In a fluidised bed reactor, the syngas is heated up before it is exposed to the catalyst.

761 Fluidised bed reactors possess higher heat exchange efficiency compared to fixed bed reactor

762 due to the circulating flow design. The construction of the reactor is also simpler which greatly

763 reduced the overall production cost. On the other hand, catalyst removal from the reactor is

764 also simpler which reduces maintenance time. However, expensive scrubbing system is needed

765 to separate the small catalyst particles from the outlet gas [105,144].

766   In slurry reactors, the catalyst is suspended in the liquid where the syngas is bubbled.

767 Heat is supplied by the steam flow. Slurry reactors possess excellent heat transfer, thus

768 increases the overall process efficiency. In addition, the ease of catalyst replacement also

769 reduces production cost. The down side of it is the difficulty in separating the catalyst and wax

770 [144,145]. Different types of reactors have their own advantages and disadvantages, the

771 optimum choice depends on the final target products and operating conditions [105].

772

773 **2.6.3   Performance of FT fuel in gas turbines**

774   The use of FT fuel in gas turbines has been widely researched. Hermann et al. [146,147]

775 examined the performance of FT fuel using a Volvo Aero gas turbine (VT40). FT fuel achieved

776 higher combustion efficiency compared to Jet A-1 for equivalence ratio of 0.1 to 0.2, with a

777 maximum improvement around 2%. Meanwhile, higher NO_x (>3 g/kg) was emitted by FT fuel

778 due to higher flame temperature compared to Jet A-1 (<3 g/kg). However, NO_x emissions

779 against Jet A-1 were also found to be reduced [97,148]. Chan et al. [97] compared the

780 performance of synthetic kerosene with aromatics (SKA), FT synthetic paraffinic kerosene

781 (SPK), and 50-50 blend of Jet A-1 and hydroprocessed SPK using a turbofan engine (CF700-

2D-2). It was reported that FT fuel led to a reduction in NO_x emissions. At 80% engine loading, neat FT fuel achieved a reduction of 32% in NO_x compared to Jet A-1 due to lower primary zone temperature. The CO emissions tend to show a reduction trend when compared with conventional jet fuels [149–151]. Lobo et al. [149,150] compared the emissions of FT fuel against Jet A-1 using a CFM56-7B gas turbine engine. A reduction of 5−10% in carbon monoxide was achieved by FT fuel due to lower fuel viscosity.

Bulzan et al. [152] operated a CFM56-2C1 gas turbine engine fuelled with FT fuel and JP-8. The emission data showed that sulphur dioxide emissions for JP-8 was higher than that of FT fuel by a factor of 2. The low SO_x emissions was due to the absence of sulphur in the FT fuel. Furthermore, soot emissions have been consistently lower for FT fuels compared to baseline fossil fuels [97,100,149–155]. The reduction in soot is largely attributed to the absence of aromatic rings in the fuel [156,157].

Corporan et al. [158] studied the particulate matter emissions of FT fuel using a T63 turboshaft engine and a swirl stabilised combustor. Particulate matter (PM) emissions for neat FT fuel, blend of FT fuel/JP-8 (75/25, 50/50 and 75/25) and neat JP-8 were compared. They found that FT fuel produced the finest particle size compared to blended fuel and neat JP-8. During cruising conditions, particle mass for FT fuel was 95% smaller compared to JP-8, which was attributable to the reduction in soot nuclei. Sulphur oxide emissions for FT fuel were also lower as compared to neat JP-8. Bester and Yates [153] also reported significant reduction in soot for FT fuel by 86.8% compared to baseline fuel. The improved soot oxidation by FT fuel combustion led to reduced fluid flow frictional losses in combustor, thus contributing to an improved thermal efficiency. Thermal efficiency for FT fuel engine was increased by an average of 1.17% at cruising condition. The improvement was attributed to the higher H/C ratio of FT fuel compared to Jet A-1. Table 8 summarises the combustion tests of FT fuel conducted in gas turbine engines.

807   Transient, ignition and extinction performance of gas turbine engine powered by FT

808 fuel have been widely researched. Vukadinovic et al. [159] investigated the combustion

809 characteristic of FT fuel, Jet A-1 and aromatics-enriched FT fuel using a combustion vessel.

810 Although all of the tested fuels exhibited similar laminar flame velocity for equivalence ratios

811 0.6 - 1.5, the extinction resistance characteristic for FT fuel was observed to be stronger than

812 that of Jet A. Conversely, Moses et al. [154,155] found no distinct difference in the ignition

813 and extinction performance for synthetic jet fuel and Jet A-1. The study was conducted using

814 a Pratt & Whiney JT-9D engine with a series of take-off cycles was imposed on the engine.

815 There was no significant degradation on engine performance when using synthetic jet fuel. In

816 addition, synthetic jet fuel showed nearly 22% droplet size reduction against Jet A-1 at -40 °C.

817   Davidson et al. [160] showed that neat FT fuel was more fuel efficient than Jet A-1 in

818 a test using a General Electric CF-700-2D-2 engine. At 80% engine loading, the neat FT fuel

819 achieved 113.5 kg/kN-hour specific fuel consumption, while Jet A-1 achieved 114.5 kg/kN-

820 hour. For transient testing, FT fuel showed slightly slower shaft speed acceleration as compared

821 to Jet A-1. In another testing using TRS-18 gas turbine engine, Davidson et al. [161] reported

822 that there was no significant difference in transient shaft acceleration between FT fuel and Jet

823 A-1. Meanwhile, all fuels tested showed comparable specific fuel consumption at steady state

824 conditions. In real flight tests, synthetic jet fuels showed no obvious sign of engine performance

825 deterioration. Transient engine speed acceleration was comparable to baseline fossil jet fuels

826 [162,163]. The findings were consistent with laboratory testing, implying that FT fuel is a

827 viable alternative jet fuel.

828

829

830   **3.0   Considerations of alternative fuels as gas turbine fuels**

The inferior viscosity of SVO restricts its usage in existing gas turbine system. Fuel preheating is an effective method to reduce the fuel viscosity. The use of twin-fluid atomiser and elevating the ALR can be deployed to atomise the viscous SVO [14,43,44]. Other atomisation techniques such as flow-blurring atomisation [39] and superheated steam atomisation [40] may be incorporated into fuel preheating system to improve atomisation quality. Nonetheless, comprehensive studies are needed as these techniques are still widely under-researched, leading to a lack of thorough understanding on the overall effect on gas turbine operation.

Although combustion performance of SVO can be potentially improved via advancement in fuel delivery and atomisation technologies, extensive use of SVO may lead to adverse environmental and socioeconomic effects. Ji and Long [164] concluded from their study that overwhelming land occupation for feedstock plantation of first generation SVO causes habitat fragmentation and bio-invasion. Furthermore, Koizumi [165] reported a direct competition between agricultural based biofuel feedstock and food production. Elevating the production of agricultural based biofuel feedstock also gives rise to the cost of agricultural commodity [165]. The advantages of SVO include the simple production process, storage ease and near zero toxicity. However, the use of SVO should not be prioritised for large-scale power generation as the fuel used will divert food away from the market and incurs adverse ecological dilemma.

Direct usage of bio-oil in gas turbine is also limited by its high viscosity. Moreover, the high bio-oil acidity level, high particulate matter (PM) emissions, solid deposition on turbine due to the presence of trace elements and fuel nozzle blockage during operation are additional drawbacks that inhibit direct bio-oil usage in gas turbine [140]. Thus, upgrading the physical properties of bio-oil is a more promising approach to expedite its mainstream application in gas turbine. Among many types of upgrading methods, esterification/solvent addition is

856   undoubtedly the most practical way of enhancing the physical properties of bio-oil owing to its

857   simplicity and involves substantially lower cost [128]. Alcoholic fuels, diesel and biodiesel are

858   possible solvents that have been proposed [166,167]. Nonetheless, endeavour studies are

859   required to acquire overall understanding on the effect of blending ratio on gas turbine

860   performance, long term operation and material compatibility.

861   Bio-oil can be produced from a variety of organic feedstock such as lignocellulosic,

862   plant and agricultural waste. Diversified bio-oil feedstock minimises its negative

863   socioeconomic and ecological impacts. Nonetheless, physical properties of bio-oil produced

864   from different feedstock are varied. Spray combustion characteristics and emission

865   performance of bio-oil are greatly affected by its compositions such as ash, tar, char, water and

866   nitrogen contents. Comprehensive studies are needed to characterise their individual influence

867   on gas turbine performance. Bio-oil specifications for various gas turbine applications can be

868   subsequently formed based on parametric studies.

869   For bioethanol, current findings show that is cleaner than fossil-based fuels with

870   considerable lower emissions of NO, CO and UHC at identical thermal output power [124].

871   The calorific value of bioethanol is inherently lower than diesel and natural gas, thus increasing

872   fuel supply to achieve the identical thermal output power with fossil fuels could undesirably

873   elevate the overall operating cost. Instead of totally replacing fossil fuel, bioethanol can be used

874   as supplementary fuel to be blended with conventional or more viscous fuels. Choi et al. [168]

875   blended ethanol with biocrude-oil and showed a reduction in CO emissions against neat ethanol

876   and biocrude-oil. Martin and Boateng [169] reported that blending switchgrass pyrolysis oil

877   with ethanol in 20/80 ratio by weight achieved comparable CO emissions with neat ethanol but

878   the NO emissions increased considerably. Table 9 compares the feasibility and considerations

879   of different alternative fuels as gas turbine fuels.

880   Biodiesel has shown to be a viable biofuel in industrial gas turbine in view of its

881   comparable properties with conventional fuels. The stringent requirement of jet fuel

882   compliance limits the application of biodiesel in aviation-based gas turbine, as shown in Table

883   10. Land-based industrial gas turbine is fuel-robust by design, allowing the use of biodiesel.

884   The similarity in physical properties between biodiesel and diesel enables the application of

885   the former in gas turbine with minimal modification to the existing system. Gas turbine

886   manufacturers have introduced fuel-flexible gas turbine that allows the usage of biodiesel

887   [12,13]. Present studies focus heavily on first and second-generation biodiesels. The shifting

888   trend into third generation biofuel uptake prompts future research to investigate the combustion

889   characteristics of biodiesel made from third generation feedstock such as algae.

890   Despite the successful test flights with HVO/jet-fuels blends ascertaining its capability

891   for future aviation and power generation industries [171], current studies provide only limited

892   understanding on HVO combustion characteristics in gas turbine. Owing to the difference in

893   chemical composition against conventional jet fuels, thorough understandings on fundamentals

894   HVO combustion characteristics is essential, which include properties such as flame speed,

895   extinction, reactive species quantification effects on combustion performance [172].

896   Furthermore, assessment of HVO life cycle analysis is also important. Depending on the

897   feedstock types, CO_2 life-cycle for HVO can vary significantly [171]. This is primarily due to

898   HVO being produced from SVO at present stage [94]. Apart from SVO, it was also reported

899   that bio-oil can be converted into HVO via hydrodeoxygenation process [93,94]. This

900   inherently minimises its negative socioeconomic and ecological impacts since wide variety of

901   organic matters can be used as feedstock for producing bio-oil [94,132]. Nonetheless, technical

902   difficulties currently faced by hydrodeoxygenation process include optimum catalyst selection

903   for bio-oil from different feedstock [94]. The optimum temperature selection is another key

904   element in hydrodeoxygenation process to eliminate oxygen contents and elevating the

905   calorific value of HVO produced [94]. In essence, HVO shows comparable physical properties

906   and combustion performance to conventional jet fuels, but sustainable feedstocks such as bio-

907   oil, second and third generation feedstock should be prioritised for future HVO production.

908   FT fuel has demonstrated superior emissions, transient, ignition and extinction

909   performances against fossil-based jet fuels. Despite the proven feasibility of FT fuel as

910   alternative jet fuel [173], the high production cost prohibits its wide usage. Biomass is regarded

911   as cleaner feedstock option as compared to coal. It is projected by the International Air

912   Transport Association (IATA) [173] that the cost of synthetic jet fuels will approach those of

913   conventional jet fuels by year 2030 due to the climate change policies that favours

914   diversification of energy sources and lower production cost.

915

916   **4.0   Conclusions**

917   The production methods and properties of six potential alternative liquid biofuels for

918   gas turbine and their combustion performances have been reviewed. HVO and FT have

919   physical properties that resemble jet fuels. The long-chain hydrocarbon of FT fuel and HVO

920   has no oxygen molecule and contains energy density similar to that of jet fuel. The main

921   advantage of these fuels is low pour point that enables application in aviation gas turbine

922   especially at high altitude. Aviation gas turbine tests have shown comparable performance as

923   jet fuel with improved particulate matter emissions. Extensive use of FT fuel and HVO at

924   present stage is mainly inhibited by the high production cost. Biodiesel has slightly poorer

925   physical properties as compared to conventional fossil fuel, notably lower energy content,

926   slightly higher viscosity and density and high pour point. However, biodiesel tend to exhibit

927   cleaner combustion characteristics, as shown by the lower NO_x, CO and soot emissions. The

928   fuel-bound oxygen content can assist local combustion and prohibits the formation of soot.

929 Biodiesel is a good fuel candidate for stationery gas where the requirement is less stringent as

930 compared to jet fuels.

931   SVO and bio-oil are potential fuels for micro gas turbines, but the inherent nature of

932 high viscosity and density may result in fuel flow delivery and clogging of atomizer orifice.

933 Modified fuel delivery system with heating capability and improved atomisation technique can

934 be applied to overcome the limitations of the fuels. Bioethanol is another possible choice of

935 biofuels for gas turbine. The properties of bioethanol differ significantly from diesel as the

936 former has low flash point, low viscosity and high vapour pressure. Application of this fuel in

937 gas turbine requires modification in the fuel delivery and fuel storage systems. Studies of

938 bioethanol in gas turbine are relatively scarce although the fuel is widely applied in

939 reciprocating gasoline engine. This review shows that the robust nature of gas turbine and the

940 development of multi-fuel capable gas turbine enable operation with biofuels. This approach

941 is beneficial to the operators from the standpoint of meeting emission targets and reducing

942 operating costs.

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948

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