SRCA: a mild catalyst-free biodiesel process

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Abstract (300 word limit)

Statement of the Problem: Biodiesel generated from oil is an attractive biofuel, while the high production cost hinders its development. As the cost of raw materials accounts for about 70% of the total production cost, using low-grade but cheap feedstock is an effective way to reduce cost. Low-grade oils usually contain high content of free fatty acids (FFA), water and unsaponifiable matters. These impurities make it impossible to converted low-grade oils to biodiesel via homogeneous alkali or heterogeneous catalyst catalyzed process. Supercritical methanolysis (SCM) technology which doesn't require the presence of catalyst has shown its adaption to low-grade feedstocks and friendliness to environment. Though SCM technology exhibits good feedstock flexibility, fast reaction rate and high product yield, the harsh reaction conditions (～ 350 ℃ , ～ 20MPa) preclude its commercialization. The purpose of this study is to introduce a mild catalyst-free biodiesel process which is also suitable for low-grade feedstocks and easy to industrialize. Methodology & Theoretical Orientation: The mild catalyst-free biodiesel process (named SRCA process) has been explored on laboratory continues devices and tested in a 2000t/a pilot-plant. Engineering and scale-up problems have been studied and verified in the pilot-plant and a 60000t/a industrial unit. Various oils, including crude plant oils, acid oils, waste cooking oils, PFAD etc. have been used to examine the feedstock flexibility. Findings: FFAs and glycerides in low-grade oils can simultaneously react with methanol in SRCA process under mild conditions (＜280℃, ＜10MPa) . With appropriate heat transfer technology and product separation technology, most tested oils can be converted to biodiesels with high yield. The standard coal consumption of the commercial unit is 145.36 kg/t biodiesel. Conclusion & Significance: The mild catalyst-free process has been proved from laboratory to commercial scale, so it's worthy to be applied in more factories.

Image

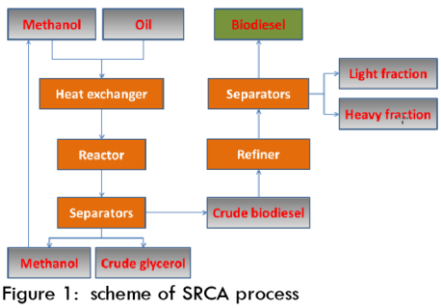


Figure 1: scheme of SRCA process



Figure 2: Devices from laboratory to pilot-plant (2000t/a) and commercial (60000t/a) scale

Table 1: Characteristics of some feedstocks tested and production yields in different scales

Feedstock	Characteristics: Acid value/ (mgKOH/g)	Saponifiable matters/%	Moisture /%	Solid /%	Colloid /%	Scale	Production yield/%
Soybean acid oil	139.7	93.6	1.9	0.3	4.2	laboratory	95.7
						pilot-plant	94.9
Palm acid oil	129.6	95.3	1.8	0.2	2.7	laboratory	96.8
						pilot-plant	97.1
Rape acid oil	108.3	89.2	2.5	0.5	7.8	laboratory	90.6
						pilot-plant	94.6
Cooking oil 1	28.4	93.9	2.3	1.0	2.8	laboratory	85.9
						pilot-plant	88.2
Cooking oil 2	78.9	94.3	3.2	0.4	2.1	laboratory	94.6
PFAD	177.6	99.1	0.6	-	0.3	laboratory	97.4
Palm frying oil	6.5	97.8	0.2	0.5	1.5	laboratory	83.4
frying Hydrogenated oil	4.5	98.5	0.2	0.7	0.6	laboratory	73.2
Mixed acid oil 1	89.0	95.3	1.6	0.01	3.1	pilot-plant	92.4
Mixed acid oil 2	51.0	91.1	0.5	0.03	8.3	pilot-plant	84.8
Mixed acid oil 3	65.2	93.3	0.6	0.76	3.58	commercial	93.7
50% Soybean acid oil + 50% frying Hydrogenated oil	72.1					laboratory	96.0
50% PFAD + 50% frying Hydrogenated oil	92.1					laboratory	95.7
30% PFAD +70% frying Hydrogenated oil	56.4					laboratory	94.9
10% PFAD +90% frying Hydrogenated oil	18.2					laboratory	83.1
60% Cooking oil 1 + 40% Cooking oil 2	52.6					laboratory	93.7
						pilot-plant	95.3
60% Soybean acid oil +40% Cooking oil 1	95.2					laboratory	95.1
						pilot-plant	94.7

Table 2: Properties of biodiesel produced from SRCA commercial [a]

Properties	Standard requirement (GB/T20828) S500	S50	Value	Test method
Density (20℃)/(kg/m³)	820~900		882.2	GB/T 2540
Kinematic viscosity(40℃)/(mm2/s)	1.9~6.0		4.487	GB/T 265
Flash point (closed)/℃	≤130		167	GB/T 261
Cloud point/℃	Report		0	SH/T 0248
Sulfur/ppm, max	0.05	0.005	0.0024	GB/T 0689
10% steamed residual carbon /%	≯0.3		0.2	GB/T 17144
Sulfated ash /%	≯0.020		0.012	GB/T 2433
Water /%	≯0.05		0.01	SH/T 0246
mechanical impurity	NO		No	GB/T 511
Copper Corrosion (50℃,3 h)	≯1		1a	GB/T 5096
Cetane number	≯49		50.5	GB/T 386
Oxidation stability (110℃)/h	≮6.0e		17.1[b]	EN 14112
Acid value /(mgKOH/g)	≯0.80		0.27	GB/T 264
Free glycerin/%	≯0.020		0.004	ASTM D 658
Total glycerin /%	≯0.240		0.03	ASTM D 658
Distillation temperature (90% recovered)/°C	≯360		343	GB/T 6536

(a) The feedstock is the mixed acid oil 3 in Table 1
(b) With antioxidant

Table 3: Consumption data of the industrial demonstration unit (per ton biodiesel)

Item	Value	Item	Value
Acid oil [a]/kg	1145.29	Electricity/kWh	109.76
Methanol/kg	124.74	Light fuel oil/kg	15.85
Fresh water/kg	42.78	Heavy fuel oil/kg	17.24
Steam (2.0 MPa)/kg	879.78	Electricity/kWh	109.76
N_2(standard state)/m³	0.137		

(a) Saponifiable matters content is 93.25%.

Recent Publications (minimum 5)

1. TanKT, LeeKT, MohamedAR, DuicN, GuzovicZ (2011) Potential of waste palm cooking oil for catalyst-free biodiesel production. Energy, 36(4): 2085-2088.
2. SakaS, IsayamaY, IlhamZ, XinJ (2010) New process for catalyst-

free biodiesel production using subcritical acetic acid and supercritical methanol. Fuel, 89(7): 1442-1446.

3. MarulandaVF, AnitescuG, TavlaridesLL (2010) Investigations on supercritical transesterification of chicken fat for biodiesel production from low-cost lipid feedstocks. Journal of Supercritical Fluids, 54(1): 53-60.
4. HayyanA, AlamMZ, MirghaniMES, KabbashiNA, HakimiNINM, SiranYM, TahiruddinbS (2011) Reduction of high content of free fatty acid in sludge palm oil via acid catalyst for biodiesel production. Fuel Processing Technology, 92(5): 920-924.
5. HayyanA, AlamMZ, MirghaniMES, KabbashiNA, HakimiNINM, SiranYM, TahiruddinbS (2010) Sludge palm oil as a renewable raw material for biodiesel production by two-step processes. Bioresource Technology, 101(20): 7804-11.
6. SakdasriW, SawangkeawR, NgamprasertsithS (2015) Continuous production of biofuel from refined and used palm olein oil with supercritical methanol at a low molar ratio. Energy Conversion & Management, 103(3): 934-942.
7. NgamprasertsithS, LaetoheemC, SawangkeawR (2014) Continuous production of biodiesel in supercritical ethanol: a comparative study between refined and used palm olein oils as feedstocks. Journal of the Brazilian Chemical Society, 25(25): 1746-1753.
8. FarobieO, YanagidaT, MatsumuraY (2014) New approach of catalyst-free biodiesel production from canola oil in supercritical tert-butyl methyl ether (mtbe). Fuel, 135(135): 172-181.



Biography (150 word limit)

Dr. Jianli Zeng is a senior engineer of the long-term project research department in Research Institute of Petroleum Processing, Sinopec. He mainly focuses on biodiesel preparation and its applications in fuel or fine chemical fields. Dr. Zeng spent over 10 years on biodiesel research and his latest achievement was the invention of SRCA-II process which had been verified in a 2000 t/a pilot plant.

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Notes/Comments: