ISSN: 0971-1260

Vol-22-Issue-16-August-2019

An Account of Process Parameters For Biodiesel Production

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Abstract

The growing problem of the carbon dioxide discharges and energy security worries has reinforced the attentiveness in alternative, nonpetroleum-based sources of energy. Biomass is the main appropriate and sustainable essential energy asset that can give elective transportation fuel, for example, bioethanol or biodiesel for the time being Biodiesel refers to vegetable oil or animal fat-based diesel fuel consisting of alkyl (methyl, propyl, or ethyl) esters. Biodiesel can be produced by the reaction of an ester with an alcohol in the presence of a catalyst affording a new ester and a new alcohol (glycerol) is called alcoholysis or transesterification. The transesterification reaction is affected by various experimental parameters, such as molar ratio of alcohol to oil, catalyst percentage, reaction time and as well as the reaction temperature. These parameters have to be considered to improve the yield of biodiesel. Higher alcohol to oil ratio is primarily used to shift the equilibrium of the reaction in the direction of the product and to achieve a higher yield from the transesterification of vegetable oil.

Key Words: Biodiesel, Gum Content, Alcoholysis

The decreasing trends of petroleum crude reserves and detrimental environmental concerns due to excessive greenhouse gas emissions (GGH) while used as fuel for transportation has threatened the industry, overall energy sector and human civilization [1]. Even at the beginning of the 21st century the transportation sector is mostly dominated by the petroleum based liquid fuels. Moreover, major parts of the chemical industry are mostly dependent upon the refinery based feedstock [2]

Biomass includes all the carbon containing waste generated from various human and natural activities. All the photo-synthetically generated materials are included under biomass [3]

 ISSN: 0971-1260

Vol-22-Issue-16-August-2019

Biomass derived energy is the second most primitive source of energy used by human civilization. In fact, the civilization has started since the humans learnt to use the biofuel for heating purposes. Prof Melvin Kelvin the inventor of Kelvin Cycle stated after his discovery that in the years to come, the need of hydrocarbon based fuel could be fulfilled by biomass alone [4] In that regard there are several advancements of technology, how biomass energy can be derived from different biomass precursors. A schematic view of different biomass materials and their conversion technologies are presented in Fig. 1.

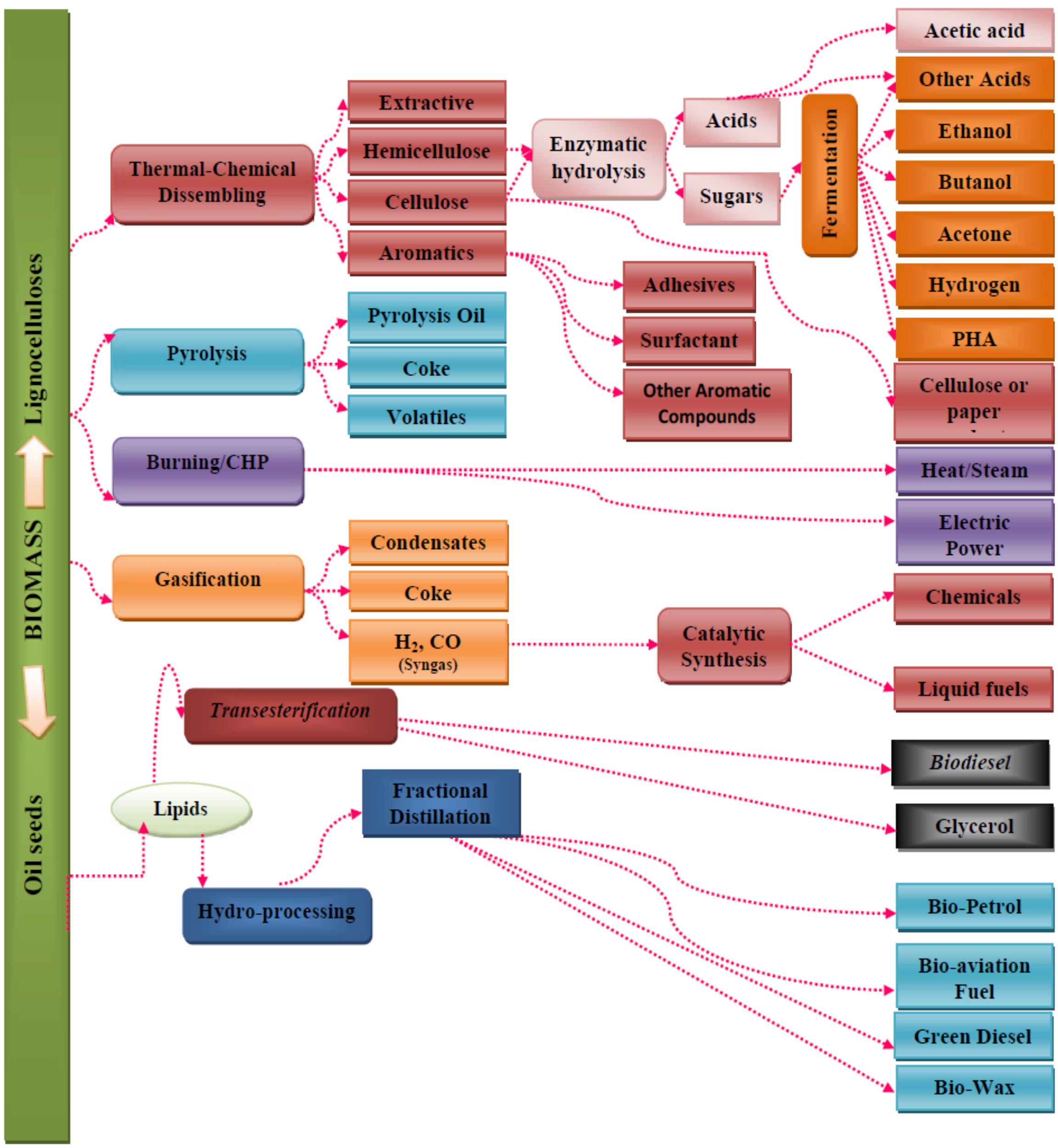


Fig.1 A Schematic View of Bio-Refinery Based on Different Biomass Precursors

The modern concept of bio-refinery can be visualized from the adaptation of any one scheme of conversion, technology as opted from the Fig.1, if the process is economically viable [5].

Liquid Biofuels

Bioethanol (C_2H_5OH)

Liquid biofuel which can be formed from numerous different biomass raw materials and transformation technologies. Orthodox raw materials utilized for the production of ethanol vary from sugar in Brazil, cereals in the USA, molasses in India and sugar beet in European nations via fermentation techniques [6].

Bioethanol can be an efficient option to fossil fuel because it is a renewable bio-mass based liquid with a boiling point 78.37 ^{o}C. Moreover, bioethanol is oxygenated in nature and therefore it serves to increase the potential of reducing particulate emissions in compression–ignition engines since it settles inside the boiling range of gasoline [7]. It can be used in existing SI engine blending with gasoline or in modified engine as a neat fuel. [8-10]

Bio-Butanol (C_4H_9OH)

It is mostly produced by the process of ABE fermentation from the algae and other biomass materials. The number carbon atoms present in any molecule is directly proportional to its energy content. It can be blended with gasoline as its boiling point is 117.4 ^{o}C and produces better air fuel mixture than gasoline-ethanol blend for SI engine. [11-12]

Vegetable oil (Triglycerides) derived biofuel

Rudolf Diesel (1912) first employed Arachide (Peanut) oil for the successful run of diesel engines. Only, afterwards it was found that direct use of vegetable due to its high viscosity and lower volatilities creates problems for diesel engine. Therefore, vegetable oils and animal fats must be subjected to one of the following chemical treatment to reduce the viscosity and facilitate utility as liquid fuel substitutes.

Biodiesel

Biodiesel can be produced by the reaction of an ester with an alcohol in the appropriate molar ratio, in the presence of a catalyst at a particular temperature and reaction time depending

ISSN: 0971-1260

Vol-22-Issue-16-August-2019

upon other process variables, [13]. This is a three step reversible reaction. The scheme of transesterification and subsequent reaction pathways are as shown in Fig. 2 and3 respectively:

The rate of the reaction (k_1, k_1', k_2, k_{-2}' and k_3, k_{-3}') is dependent upon the feedstock (oil and alcohol, types and molar ratio), process variables (temperature, pressure, reaction time, stirring speed, types of reactor etc) and amount and type of catalyst used.

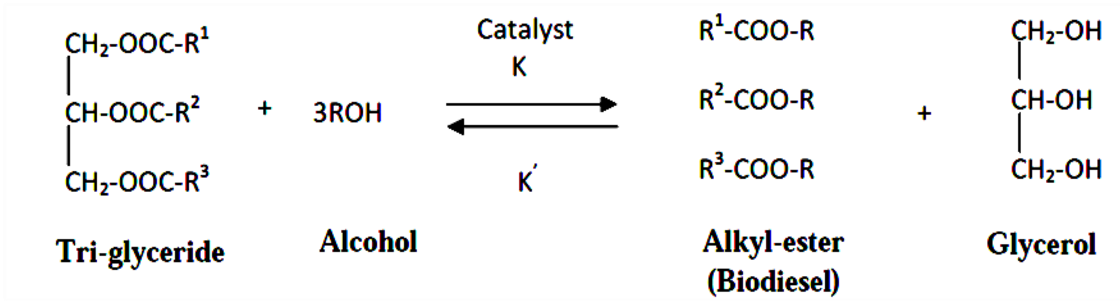
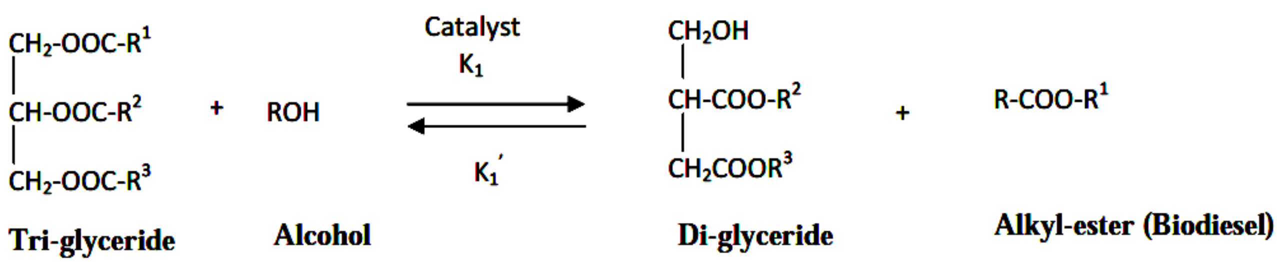
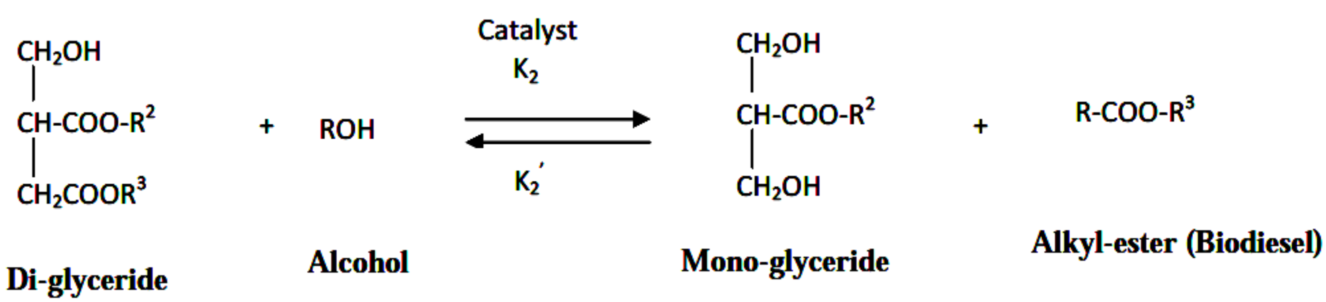


Fig. 2: Basic Transesterification Reaction

Step-1



Step-2



ISSN: 0971-1260

Vol-22-Issue-16-August-2019

Step-3

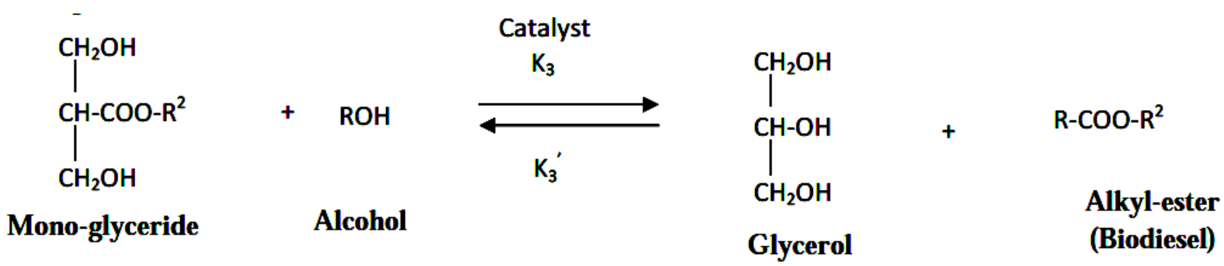


Fig. 3: Three Steps of Transesterification Reaction

The main advantages of biodiesel over fossil fuels are its higher biodegradability portability, renewability, lower sulfur, aromatic content, and higher cetane number. Biodiesel has significant potential as an alternative of conventional fuel in compression ignition (CI) engines as a substitute of petroleum derived diesel due its similarity of volatilization (boiling point) with petroleum diesel [13]

Blending

Fuel blending is the blending of fuel with any other substance or substances. Generous blends of biodiesel and fossil diesel are most commonly distributing products in the retail diesel fuel market. Percentage amount present of biodiesel in any fuel mixture is represented by term 'B'. For example, B20 represents fuel containing 20% biodiesel and 80% crude petroleum diesel oil. This mixture can be employed directly in diesel engines. These blends can be prepared by mixing of pure biodiesel i.e. B100 varying percentage as desired with petroleum diesel at manufacturing site or any other location as desired. The advantage of blending is liquid nature-portability but the viscosity of neat vegetable oil cannot reduce much, thus requiring biodiesel.

Pyrolysis

It is a simple form of thermal cracking with following reorganization of parts. It involves heating in the absence of air with the help of appropriate catalyst. SiO_2, molecular sieves, zeolites, sodium carbonate and Al_2O_3 etc. are some widely used catalyst for pyrolysis. The resulting biocrude can then be used as fuel or for the production of chemicals and other ''bio-based'' products. [14]

ISSN: 0971-1260

Vol-22-Issue-16-August-2019

Micro emulsions

In this process high viscosity vegetable oils are mixed with solvents such as methanol, ethanol and 1-butanol the mixer is known as micro-emulsion. The performance of ionic or non-ionic micro emulsions was found to be similar to diesel fuel. [15]

Hydro-processing

Hydroprocessing is a refinery based technology used to convert higher molecular weight crude oil into low molecular weight compounds. Another important function of hydroprocessing is to remove sulfur, nitrogen and metals from crude oil etc. It is intended to convert saturated paraffin from triglycerides derived from biomass oils. Engine compatibility, resemblance with crude refinery and feed stock are major advantages of hydroprocessing. However, its dependency on hydrogen, expensive catalyst, and difficulty to select catalyst with respect to desired product are major drawbacks of this technology. [16]

It is obvious from above discussion that biodiesel is the ideal alternative for diesel engines (C.I.) in current scenario. The biggest encouragement to employ biodiesel is its environmental benefits and easy processing. Biodiesel burns smoothly than petro-diesel due to its inherent oxygen. A few literature reviews [17,18] of the current era establish the fact that among the above discussed methods for processing vegetable oil as fuel, namely, microemulsion, hydro-processing and transesterification, the latter is the most popular and preferred due to several attributes. However, the selection of appropriate transesterification process variables requires a lot many experimental works that varies depending upon the reactants (oil, alcohol), process variables and catalyst used.

Factors Affecting Transesterification Process for Biodiesel Production

Oil composition and Free Fatty Acids (FFA)

Utmost of the industrial biodiesel is formed from vegetable [19-21]. The fatty acid profile of the typical oil used for transesterification should also be suitable. For example, Leenseed oil cannot be used for transesterification due to the presence of high olefinic bonds. Fatty acid profile of some of the commonly used vegetable oils for biodiesel purposes are as listed in Table-1.

ISSN: 0971-1260

Vol-22-Issue-16-August-2019

Table 1: Typical Fatty Acid Profile of Oligogeneous (Tri-glyceride) Feedstock [22]

S.N.	Oligogeneous (Tri-glyceride) Feedstock	Palmitic Acid	Palmitoleic acid	Stearic acid	Oleic acid	Linoleic acid (18:2)	Linolenic Acid (18:3)
1	Corn Oil	6.0	-	2.0	44.0	48.0	-
2	Canola oil	4.00	<1	2.00	62.00	20.00	9.00
3	Coconut oil	9.80	-	3.00	6.90	2.20	-
4	Cottonseed	28.3	-	0.9	13.3	57.5	-
5	Olive	14.6	-	75.4	10.0	-	-
6	Palm	42.6	0.3	4.4	40.5	10.1	0.2
7	Peanut	11.4	-	2.4	48.3	32.0	0.9
8	Rapeseed	3.5	0.1	0.9	54.1	22.3	-
9	Safflower	7.3	0.1	1.9	13.5	77.0	-
10	Soybean	11.9	0.3	4.1	23.2	54.2	6.3
11	Sunflower	6.4	0.1	2.9	17.7	72.9	-
12	*J.curcus*	14.2	0.7	7.0	44.7	32.8	0.2
13	*P.pinnata*	10.2	-	7.0	51.8	17.7	3.6
14	*M.Indica*	24.5	-	22.7	37.0	14.3	-
15	Fish oil	10.10	0.10	4.40	26.90	51.80	0.40

Temperature of reaction

The speed of transesterification reaction is widely inclined by the temperature at which the reaction is proceeding. A higher reaction temperature can be instrumental in reducing reaction time and decrease the viscosities i.e. increase in reaction rate. If the reaction temperature surpasses optimum temperature, the saponification reaction of triglycerides starts which decreases the yield of biodiesel product during homogeneous alkali catalyzed transesterification reaction [23]

ISSN: 0971-1260

Vol-22-Issue-16-August-2019

Alcohol to Triglyceride Molar Ratio

The molar ratio of alcohol to triglyceride is very important factor for effective yield of biodiesel. Three moles of alcohol and one mole of triglyceride is required for the production of three moles of fatty acid ester and one mole of glycerol in stoichiometric terms. It is suggested by many researchers to use higher alcohol to triglyceride molar ratio so that maximum ester conversion achieved. [24,25]

Reaction Time

In general reaction is completed within 90 minutes and biodiesel yield remains constant with a beyond increase of reaction time until the start of backward reaction. Backward reaction results in loss of ester as well as to initiate the saponification reaction. [19]

Water Content

Water causes problems not only during the production of biodiesel but also in purification and storage and in combustion as well. In alkali-catalyzed transesterification reaction, water causes decrease in biodiesel quality as it lowers heat of combustion, corrosive in nature and catalizes hydrolytic reaction. [20]

Speed of Agitation

Speed of agitator or stirring speed is an important factor for transesterification reaction. High speed of agitation is suggested for complete reaction.

Gum content

Gum content in the oil sometime affects the transesterification due to oxidation and polymerization during reaction.

Type of reactor

Different kinds of reactor were found instrumental for biodiesel production in laboratory scale and bench scale applications. [29] investigated the transesterification of rapeseed (RO) and waste sunflower (SO) oils with methanol using KOH as a catalyst, in a batch reactor of capacity. [30] used a novel continuous fix bed reactor. [23]. It is further stated that different operational parameters require different types of reactors based upon the feedstock used.

ISSN: 0971-1260

Vol-22-Issue-16-August-2019

Catalyst Type and Loading

Catalyst accelerates the reaction lowering the activation energy. Alkali catalysts include homogeneous Alkali catalysts and heterogeneous Alkali catalysts. (Fig -2) Frequently employed homogeneous Alkali catalysts are sodium hydroxide, potassium hydroxide and their alkoxide. Homogeneous alkali-catalyzed transesterification is much rapider than acid-catalyzed transesterification. Huge amount of water is needed in the process this makes this process costlier [20]

Heterogeneous catalyst for transesterification of vegetable oil has received a new dimension since last few years with greater emphasis from the world community to produce and utilize biodiesel as a partial substitute of petroleum diesel [21]. Among the solid acid catalytic transesterification sulphated zirconium could be effective as reported in several literatures [23]. Among the base heterogeneous catalyst SrO has been considered as a very effective one for transesterification. Recently, FAME yield of 99.8% was reported under Micro-Wave irradiation of 1100W output with magnetic stirring using SrO as catalyst by Koberg *et al.*, (2011) [24], at about 10s.

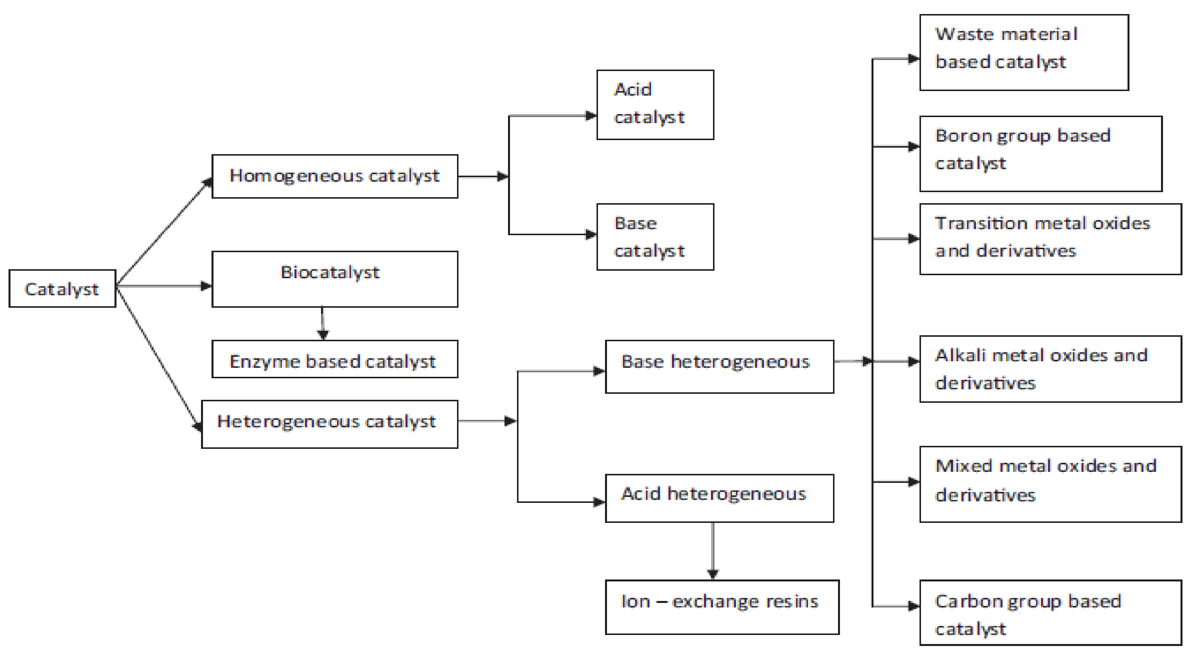


Fig.2 Flow chart of classification of catalyst

A fresh dimension of biodiesel research is the effective and cost-effective use of Bio-Based waste products from different sectors and biomass with non-homogeneous structure. The feasible solution of heterogeneous catalytic transesterification can also be looked after by combining these renewable, waste materials and traditional heterogeneous catalysts. Like Fish Shell Ash, Egg Shell waste etc. [25]

Conclusion

Optimum conditions are difficult to find, in-general trial and error method is applied to find them. Even though it can be concluded that Reaction Time, Type of Catalyst and loading, and Alcohol to Triglyceride Molar Ratio are most dominating parameters for biodiesel production.

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Vol-22-Issue-16-August-2019

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