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An Investigation on Fatty Acid Compositions of Three-Generation Biodiesel Fuels

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Abstract: Biodiesel's fuel properties affecting engine performance, combustion and emission characteristics significantly depend on the feedstock from which it is produced. The most important parameter which influences the feedstock properties is its fatty acid composition. Fatty acid chain length, unsaturation level, and the type of unsaturated bonds have significant impacts on the feedstock and therefore on biodiesel fuel properties. Biodiesel is generally divided into three generations, depending on its feedstock. In this experimental study, twelve different biodiesel fuels covering three generations were produced, their fatty acid distributions were determined and compared with each other. It has been determined that the biodiesel obtained from coconut oil had quite different fatty acid distribution compared to other biodiesel fuels. Coconut biodiesel, palm biodiesel and cottonseed oil biodiesel fuels were in the first three order in terms of saturated fatty acid content, while algal oil biodiesel had the lowest saturation level.

Keywords: Biodiesel, Feedstock, Fatty acid composition, Fuel property.

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INTRODUCTION

Together with industry and households, transportation sector is one of the main factors causing very high energy consumption and environmental pollution. Despite many economic and geopolitical problems in the world, energy demand of transportation sector has been increasing each year. Meeting this energy need is crucial for the continuity of the global supply chain. The current problems in reaching fossil energy sources has revealed the vital significance of sustainable and domestically producible alternative energy resources much more clearly. The use of alternative energy in the transportation sector is an issue that should be strongly emphasized in terms of sustainable and environmentally friendly transportation. Nowadays, electrification in the automotive industry is a very popular issue and is expanding rapidly. However, there are many technical problems that should be solved, especially in medium-heavy duty vehicles and working machines. In addition, the unit price of electricity to be consumed in these vehicles and the regulations on taxation are not clear yet. Biodiesel is a very important alternative energy source since it can be used in all areas of transportation sector including sea and airway. It is compatible with the existing fuel distribution and station network, and does not require a significant change in the fuel and injection systems of the vehicles. Infrastructure investment can be made with smaller budgets compared to other alternative energy sources. As biodiesel can be produced from domestic feedstocks, it can alleviate the dependence on the import energy sources causing current account deficit problem. Moreover, compared to petroleum-based diesel fuel, biodiesel has more environmentally friendly exhaust emissions (excluding NO_x) and superior lubricity property. (1-5).

BIODIESEL FEEDSTOCKS

When the related literature is examined, it is seen that the use of vegetable oils in diesel engines as fuel started with the invention of the diesel engine (6). Vegetable oils' unacceptably high viscosities which prevent their direct usage in diesel engines are significantly reduced by a chemical reaction called transesterification. Biodiesel which is an alternative diesel fuel can be produced from lots of different feedstocks. However, when today's industrial scale biodiesel production is examined globally, it is seen that edible vegetable oils such as soybean oil, rapeseed oil, palm oil, etc. are still the main feedstock of this industry. Edible vegetable oils are classified as the first generation biodiesel feedstock. Waste frying oils, waste animal fats and inedible oils can also be used as feedstock in biodiesel production. A biodiesel fuel produced from waste feedstocks or inedible vegetable oils is defined as the second-generation biodiesel fuel. Another biodiesel feedstock that is more recent than other feedstocks is algae. A biodiesel fuel of algal oil origin is called as the third-generation biodiesel (7).

The feedstock type from which biodiesel is produced has the determinant impact on the sustainability of the biodiesel industry and on the cost of biodiesel as well as on the obtained biodiesel's physico-chemical fuel properties. During transesterification reaction, the fatty acid distribution of the biodiesel feedstock remains almost constant. In other words, the fatty acid composition of the biodiesel fuel reflects the fatty acid structure of the feedstock from which it is produced, and consequently the fuel properties of different origin biodiesels show significant differences. For example, cetane number, viscosity, calorific value, and lubricity increase with increasing fatty acid chain length. Moreover, as the fatty acid saturation level increases, oxidative stability improves, whereas cold flow properties are adversely affected (8-10). In order to better understand a biodiesel fuel chemically, it is critical to understand the chemical structure of the feedstock from which biodiesel fuel is produced.

The Chemical Structure of Biodiesel Feedstocks

Biodiesel feedstocks (oils and fats) are formed as a result of the bonding (esterification) of three moles of fatty acids to one mole of glycerine with ester bonds (the bond between hydroxyl and carboxyl groups). They are also called glycerides, since there is glycerine in the formation of oil and fat. During the formation of an oil or fat molecule, three ester bonds are formed and three moles of water are released. The resulting structure is defined as triglyceride (triacylglycerol). The main chemical constituent of vegetable oils and animal fats are triglycerides. Oils and fats are composed of about 90-98% triglycerides and limited number of di- and monoglycerides (11). Triglyceride formation mechanism is shown in Figure 1.

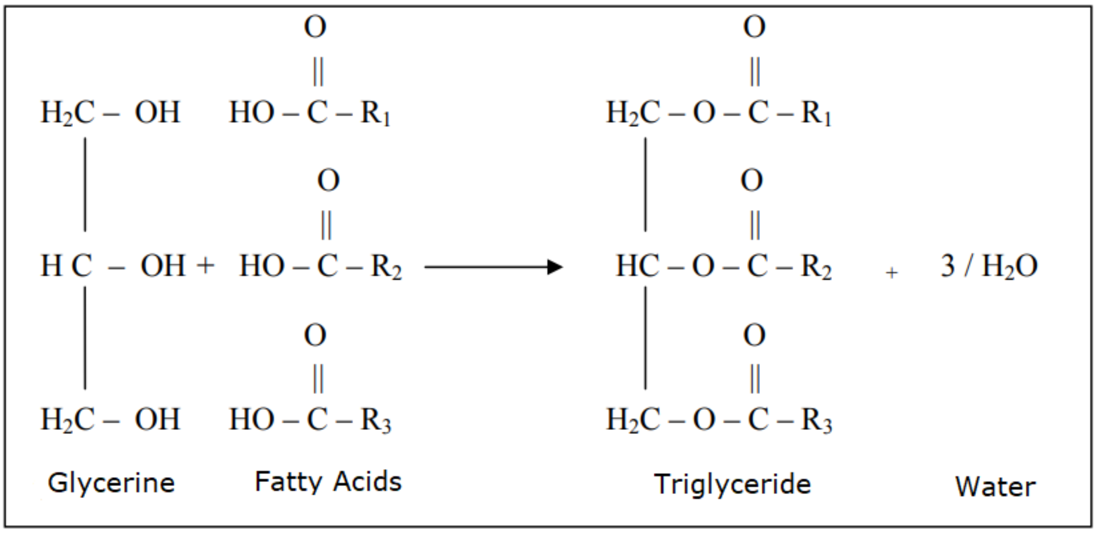

Figure 1: Triglyceride formation mechanism.

R_1, R_2 and R_3 in the figure stand for the fatty acid molecules. When the fatty acids in a triglyceride molecule are the same it is called as a simple triglyceride. They are rarely seen in the nature. If two or more different fatty acids are combined with glycerine, it is termed a mixed triglyceride (12).

Figures 2 and 3 show an example of simple triglyceride and mixed triglyceride, respectively.

In a triglyceride molecule, the mass of glycerol is about 41 grams, whereas the mass of fatty acid radicals is about 650-790 grams. These amounts show us that fatty acid radicals constitute a very big portion of the reactive groups and so they greatly affect the physico-chemical characteristics.

The importance of comprehensive analysis of fatty acids, which comprise about 96% of a triglyceride molecule, is clearly seen. Fatty acids can be defined as organic acids consisting of a carboxyl group and a straight carbon atom chain (13). The chemical structure of a fatty acid can be seen in Figure 4 at which the structural formula of undecanoic acid is illustrated.

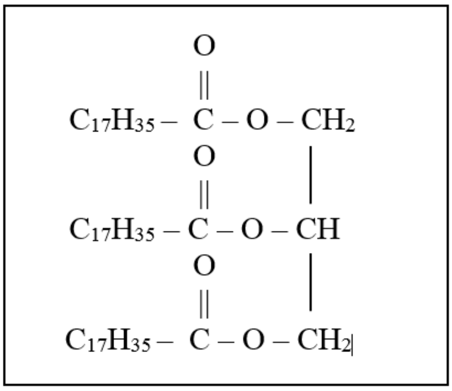

Figure 2: Simple triglyceride (tristearin).

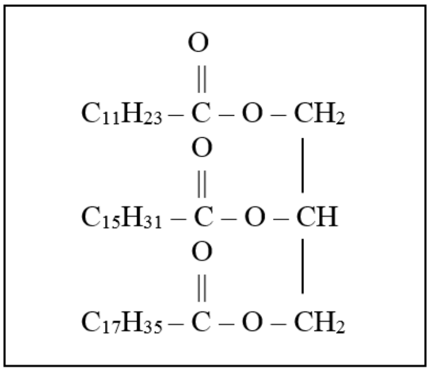

Figure 3: Mixed triglyceride (lauropalmitostearin).

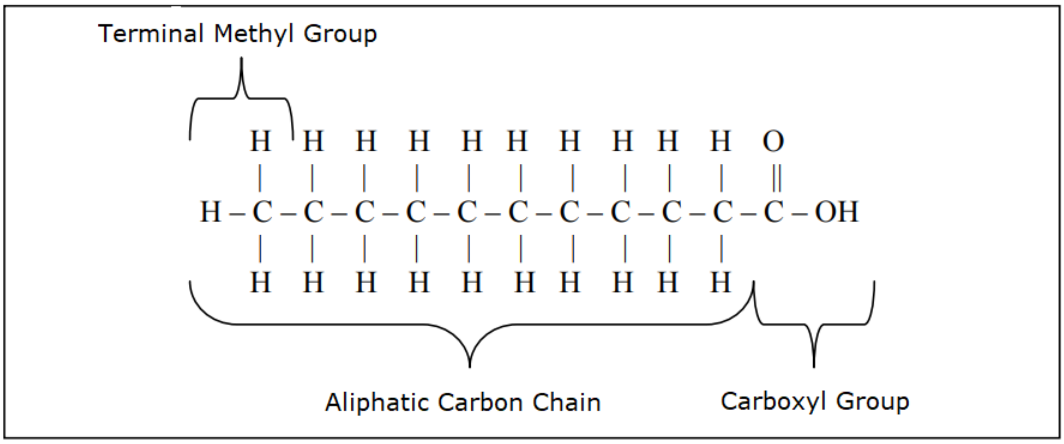

Figure 4: The chemical structure of a fatty acid.

Fatty acids differ from each other in their carbon chain length, the number and the position of double bonds. Fatty acids can be saturated at which all carbon atoms bonding each other with single bonds or unsaturated containing one or more double bonds. A fatty acid is shown by two numbers. The first number indicates the number of carbon atoms in the fatty acid chain while the second number shows the number of double bonds. For instance, C 18:2 (linoleic acid) indicates that this fatty acid has totally 18 carbon atoms and contains 2 double bonds. The some common fatty acids found in oils and fats can be seen in Table 1.

Table 1: Some common fatty acids and their chemical structures.

Fatty Acid Name	Carbon Atom :Double Bond (C:D)	Chemical Structure
Butyric Acid	C 4:0	$CH_3(CH_2)_2COOH$
Caproic Acid	C 6:0	$CH_3(CH_2)_4COOH$
Caprylic Acid	C 8:0	$CH_3(CH_2)_6COOH$
Capric Acid	C 10:0	$CH_3(CH_2)_8COOH$
Lauric Acid	C 12:0	$CH_3(CH_2)_{10}COOH$
Myristic Acid	C 14:0	$CH_3(CH_2)_{12}COOH$
Myristoleic Acid	C 14:1	$CH_3(CH_2)_3CH=CH(CH_2)_7COOH$
Palmitic Acid	C 16:0	$CH_3(CH_2)_{14}COOH$
Palmitoleic Acid	C 16:1	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$
Stearic Acid	C 18:0	$CH_3(CH_2)_{16}COOH$
Oleic Acid	C 18:1	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Linoleic Acid	C 18:2	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$
Linolenic Acid	C 18:3	$CH_3CH_2CH=CHCH_2CH=CHCH_2CH=CH(CH_2)_7COOH$
Arachidic Acid	C 20:0	$CH_3(CH_2)_{18}COOH$
Gadoleic Acid	C 20:1	$CH_3(CH_2)_7CH=CH(CH_2)_9COOH$
Behenic Acid	C 22:0	$CH_3(CH_2)_{20}COOH$
Erucic Acid	C 22:1	$CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$
Lignoceric Acid	C 24:0	$CH_3(CH_2)_{22}COOH$

If unsaturated fatty acids are examined in more detail, it will be seen that the position of double bonds can also be different. Double bond position, just like the number of double bonds, has a significant influence on the chemical reactivity. There are two different position possibilities for double bonds: in the conjugated double bond position there is no methylene (CH_2) group between the double bonds. The double bonds in the carbon chain are separated by a single bond. In the isolated double bond position, there are one or more methylene groups between the double bonds in the carbon chain. Conjugated fatty acids show quite different physico-chemical properties from isolated fatty acids having the similar closed chemical formula. Conjugated fatty acids react more easily than isolated fatty acids (14).

Another important issue that needs to be emphasized in terms of double bond configuration is the *"cis"* and *"trans"* configurations. These double bond configurations also significantly affect the properties of a vegetable oil or an animal fat. In the *"cis"* configuration, the carbon chains on either side of the double bonds tend towards each other and the hydrogen atoms in the double bond are on the same side. There is a slight bend in the double bond location. Most of the unsaturated fatty acids have *"cis"* double bonds. In the *"trans"* configuration, hydrogen atoms in the double bond are on the opposite side. *"Trans"* carbon chain is almost straight. "Cis" and "trans" configuration show different properties. For example; *"trans"* fatty acids have higher melting point than *"cis"* fatty acids. The melting point of oleic acid (C18:1 cis) having *"cis"* double bond is 18.9 °C, while the melting point of elaidic acid (C18:1 trans) with a double bond in the *"trans"* configuration is 43 °C (15).

As mentioned in the previous sections, feedstock type used in biodiesel production affects not only the break-even price of the obtained fuel but also the sustainability of the biodiesel industry. Moreover, biodiesel's fuel properties are highly dependent on the feedstock from which it is produced. Fatty acid composition significantly affects the characteristics of vegetable oils and animal fats and inevitably the physico-chemical fuel properties of the biodiesel fuel produced from these feedstocks. For this reason, it is very important to determine the fatty acid composition of biodiesel fuels obtained from different feedstocks. However, the number of studies in which wide range of biodiesel fuels' fatty acid distributions are determined, comprehensively analysed and compared with each other is very limited. In this experimental study, it was aimed to partially fill this gap in the literature.

MATERIALS AND METHODS

The main goal of this experimental study was to determine the different origin biodiesel fuels' fatty acid structures on which biodiesel fuel properties are largely dependent. To make a comprehensive study, 12 different biodiesel fuels (covering three biodiesel generations) were produced from various feedstocks. Soybean oil, corn oil, safflower oil, olive oil, sunflower oil, palm oil, rapeseed oil, algae oil, cottonseed oil, hazelnut oil, waste frying oil and coconut oil were used as feedstock for biodiesel production. Transesterification reaction conditions were 6:1 molar ratio of methanol:feedstock, 1% KOH (w/w), reaction temperature of 60 ºC and 1 hour reaction duration. After the reaction was finished, the mixture was transferred into a separatory funnel and left overnight for complete glycerol phase separation. The glycerol phase was drained and the methyl ester was washed four times with distilled water at 50 °C. After the washing process, biodiesel fuel was dried at 101 °C for 1 hour. The dried fuel was filtered and then stored in the refrigerator at 4 °C. All biodiesels were observed for one week and no phase separation or bottom sedimentation problems were detected. Fatty acid distributions of all produced biodiesel fuels were determined by using IUPAC 2.301 method.

RESULTS AND DISCUSSION

Biodiesel fuels were coded as following: Safflower biodiesel fuel (SfB), waste frying oil biodiesel fuel (WFB), sunflower oil biodiesel fuel (SB), hazelnut oil biodiesel fuel (HB), rapeseed oil biodiesel fuel (RB), corn oil biodiesel fuel (CB), palm oil biodiesel fuel (PaB), cotton seed oil biodiesel fuel (CtB), soybean oil biodiesel fuel (SoB), olive oil biodiesel fuel (OB), coconut oil biodiesel fuel (CcB), and algal oil biodiesel fuel (AlB). Fatty acid distributions of all biodiesel fuels produced in this study were given in Table 2.

As seen in Table 2, biodiesel fuels produced from different feedstocks contain varying percentages of different fatty acids. Stearic acid (C 18:0), oleic acid (C 18:1), linoleic acid (C 18:2) and linolenic acid (C 18:3) were detected in all biodiesel fuels. Palmitic acid (C 16:0) was found in all biodiesel fuels except SB whereas myristic acid (C 14:0) was detected in all biodiesel fuels apart from AlB. When the table is examined, it is seen that oleic acid and linoleic acid were the most dominant fatty acids in almost all biodiesel fuels examined. The most dominant fatty acids in SfB were linoleic acid (75.59%), oleic acid (12.91%) and palmitic acid (6.65%), respectively. WFB's oleic acid (45.15%) and linoleic acid (39.74%) contents were close to each other. As saturated fatty acids, the content of palmitic acid (8.80%) was almost twice the stearic acid amount (4.20%). It also contained trace amounts of myristic acid (0.13%). Linoleic acid (54.83%) and oleic acid (33.43%) were the two most prominent fatty acids in SB. In addition, this should be underlined that, among all tested biodiesel fuels, pentadecenoic acid (C 15:1) was only detected in SB (6.46%). HB differed from all other biodiesel fuels with its octadecenoic fatty acid content of 74.24%. It was seen that the oleic acid (2.22%) and stearic acid (2.14%) contents of HB were almost the same. The most dominant fatty acids of the biodiesel fuel (RB) produced from rapeseed oil, which is the basic feedstock of the EU biodiesel industry, were oleic acid (62.13%) and linoleic acid (21.71%). Linoleic acid (52.58%), oleic acid (31.69%), palmitic acid (11.34%) and stearic acid (2.13%) were the basic fatty acids that constitute CB. The saturation level of PaB was relatively higher than other biodiesel fuels apart from CcB. The first three fatty acids of PaB were oleic acid (42.53%), palmitic acid (39.38%) and linoleic acid (10.69%). Stearic acid content of PaB (4.25) was close to those of WFB (4.20%) and SoB (4.19%). Almost all the fatty acid composition of CtB was composed of linoleic acid (56.17%), palmitic acid (21.79%), oleic acid (17.26%) and stearic acid (2.60%). Linolenic acid content (43.23%) of SoB produced from soybean oil, which is the main feedstock of the US biodiesel industry, was quite remarkable and was much higher than those of all other biodiesel fuels. The oleic acid (24.53%) and linoleic acid (21.25%) contents and also palmitic acid (6.25%) and stearic acid (4.19%) contents of SoB were quite close to each other. OB's oleic acid content (70.23%) was in the first order among all biodiesel fuels. In addition to oleic acid, OB consisted of palmitic acid (13.03%), linoleic acid (9.51%), and stearic acid (3.66%). It should be especially expressed that CcB was quite different from other biodiesel fuels terms of its fatty acid composition. It contained significant amounts of fatty acids that other biodiesels did not have. CcB's lauric acid (48.89%), caprylic acid (8.49%) and capric acid (5.85%) contents distinguished it from other biodiesels. In addition to these fatty acids, CcB contained myristic acid (19.67%), palmitic acid (7.49%), oleic acid (4.66%), and stearic acid (3.32%). It should be strongly underlined that CcB, with its saturation level of 94.42%, was by far in the first order among the 12 different biodiesel fuels examined in this study. The saturation level of PaB (45.59%), which was the second in terms of saturated fatty acid content, was almost half of CcB. As can be understood from the Table 2, the fatty acid diversity of AlB, which is classified as 3rd generation biodiesel, was more limited than other biodiesel fuels. It was determined that AlB composed of 62.09% oleic acid, 21.22% linoleic acid, 9.54% linolenic acid and 1.70% stearic acid. In addition, another issue that should be emphasized is that AlB fuel (total saturation rate of 6.41%) had the lowest saturation level among the tested biodiesel fuels.

Table 2: Fatty acid compositions of biodiesel fuels (%, w/w).

C:D	SfB	WFB	SB	HB	RB	CB	PaB	CtB	SoB	OB	CcB	AlB
C 5:0	-	-	-	-	-	-	0.04	-	-	-	0.70	-
C 8:0	-	-	-	-	-	-	-	0.01	-	-	8.49	-
C 10:0	-	-	-	-	-	-	0.05	0.01	-	-	5.85	-
C 11:0	-	-	0.10	-	-	-	-	-	-	-	-	-
C 12:0	-	-	-	-	-	-	0.49	0.07	-	-	48.89	-
C 13:0	-	-	-	-	-	-	-	-	-	-	0.01	-
C 14:0	0.09	0.13	0.09	0.04	0.06	0.04	1.04	0.60	0.05	0.02	19.67	-
C 14:1	-	-	0.02	-	-	-	-	-	-	-	-	-
C 15:0	0.02	-	-	-	0.03	-	0.05	0.02	0.02	-	-	-
C 15:1	-	-	6.46	-	-	-	-	-	-	-	-	-
C 16:0	6.65	8.80	-	5.20	5.54	11.34	39.58	21.79	6.25	13.03	7.49	4.71
C 16:1	0.07	-	0.10	0.32	0.20	0.10	0.18	0.47	0.08	0.97	-	0.20
C 17:0	0.04	-	-	0.03	-	0.07	0.09	0.07	0.06	0.14	-	-
C 17:1	-	-	-	0.08	0.07	-	0.03	0.03	0.03	0.22	-	0.06
C 18:0	3.29	4.20	3.55	2.14	1.70	2.13	4.25	2.60	4.19	3.66	3.32	1.70
C18:1[a]	0.02	-	0.02	74.24	0.04	-	0.05	0.15	0.03	-	-	-
C18:1[b]	12.91	45.15	33.43	2.22	62.13	31.69	42.53	17.26	24.53	70.23	4.66	62.09
C 18:2	75.59	39.74	54.83	14.36	21.71	52.58	10.69	56.17	21.25	9.51	0.70	21.22
C 18:3	0.12	0.20	0.05	0.11	6.65	0.92	0.24	0.14	43.23	0.54	0.05	9.54
C 18:5	-	-	-	-	-	-	-	-	0.02	-	-	-
C 20:3	-	-	-	-	0.03	-	-	-	0.24	-	-	-
C 20:4	0.02	-	0.03	-	0.02	0.02	0.01	0.02	0.02	0.02	-	0.02

a: Octadecenoic acid, b: Oleic Acid.

CONCLUSION

The physico-chemical fuel properties of a biodiesel fuel are largely dependent on the feedstock type from which it is produced. At this point, the most important parameter is the fatty acid configuration of the feedstock and so the biodiesel. Biodiesel fuels are divided into three generations according to the feedstock from which they are produced. In addition to the differences between different origin biodiesel fuels in terms of economy and sustainability issues, biodiesels of different generations will have different fatty acid contents and will inevitably and significantly show different physico-chemical fuel properties affecting engine characteristics. In this experimental study, it was aimed to compare the fatty acid distributions of various biodiesel fuels from different generations. For this purpose, 12 different biodiesel fuels (covering three generations) were produced and their fatty acid structures were determined and compared with each other. It has been observed that the investigated biodiesel fuels contained different percentages of different fatty acids in accordance with their different natures. However, it has been observed that all biodiesel fuels contained palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid (in different percentages). CcB differed from other biodiesel fuels in terms of fatty acid diversity. The biodiesel with the highest saturation rate was CcB. The high saturation value of this fuel improves its some features such as cetane number, oxidative stability, lubricity, heating value whereas leads to high viscosity deteriorating the atomization quality. Among the 12 biodiesel fuels examined in this study, AlB had the lowest saturation ratio. Since the high unsaturation level of AlB will improve the cold flow properties of this fuel compared to the other biodiesel fuels, it offers an important potential to AlB as an aviation fuel.

CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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