Hydrodynamic Cavitation Applied to Corn Oil

V. Weber[1] and K. Dölle[1*]

[1]*Department of Paper and Bioprocess Engineering (PBE), College of Environmental Science and Forestry (ESF), State University of New York (SUNY), Syracuse, New York, 13210, USA.*

Authors' contributions

This work was carried out in collaboration between both authors. Author VW wrote the first draft of the manuscript. Author KD wrote the final draft and approved the final manuscript.

Original Research Article

ABSTRACT

Shrinking oil resources increases the importance of substitutes in the form of biofuels. A variety of extraction processes for the generation of biodiesel out of vegetable based oils have been established in the last decades. This research investigates in the implementation of hydrodynamic cavitation on the molecular structure of vegetable based oils to bypass the transesterification reaction among the biodiesel refinery. Two experiment setups that differ in size and composition were used to treat Corn Oil. The decomposition of Potassium Iodide was used to proof the formation of cavitation during the experiments. The destructive effect was analyzed by GC, GC-MS and NMR technique. With the use of the last mentioned device, it was possible to identify a change in the spectrum. The formation of new peaks located in the typical chemical shift areas of Olefins indicated a destructive effect on the hydrocarbon chains. The impact on the molecular structure of the Corn Oil was obtained on a low level. Consequently, the generation of biodiesel could not be achieved but it creates the basis for further investigations.

Keywords: Vegetable oils; hydrodynamic cavitation; biodiesel.

_____

*Corresponding author: E-mail: kdoelle@esf.edu;

1. INTRODUCTION

Global oil reserves are shrinking continuously and at the same time the demand is growing [1]. To cope with these contradictory effects, the reliance on fossil fuels should be reduced and the research among possible substitutes has to be enhanced. Biodiesel deriving from vegetable oil is, as aforesaid, a substitute [2] and will probably replace petroleum diesel in the next few years. Due to the environmental advantages of biodiesel, regarded as nontoxic and biodegradable [3], it is important to figure out if the production of biodiesel can be improved. In the last decades four different ways of biodiesel production have been established. These are: direct use and blending, microemulsions, thermal cracking and transesterification [4]. The last-mentioned is the most common technique regarded as the transformation of vegetable oils into fatty acid methyl esters with the assistance of a catalyst. While lowering the viscosity this process converts the large, branched oil molecules into straight-chains to adjust their structure for diesel combustion engines [1]. The transesterification process takes the benefit of a wide array of possible catalysts. Homogenous Alkaline catalysts mixture of NaOH or KOH have been so far the most conventional ones [5]. Improvements in these process have been studied by Singh et al. analyzing the two heterogenous catalysts ZnO/zeolite and PbO/zeolite [6]. Methods that bypass the use of a catalyst in order to enhance the biodiesel production, lowering the costs and manufacturing waste have been developed. Biodiesel refinery without a catalyst can be facilitated by the 'supercritical methanol transesterification method' in which the catalyst is replaced with a pressure and temperature adjusted autoclave [3].

The aim of this paper is to investigated the effect of cavitation on the large, branched oil molecules to examine a competitive non-catalyst biodiesel refinery technique.

Michel and Kozyuk follow the guidelines and describe that cavitation is the formation and disbanding of vapor-filled gas bubbles caused by a flow narrowing [7]. If the fluid stream gets constricted the liquid will fall below the vapor pressure and initiate the formation of bubbles. These cavities will be carried away in areas of higher pressure, the vapor will condense and the bubbles collapse implosively. The collapse generates shock waves which have the impact to trigger enormous forces [7].

A lot of possible applications of cavitation as a source of energy have been examined in the last years. These are: water treatment, biotechnology, sonocrystallization and atomization [8]. Matthew R. Von Bargen has analyzed the possible use of cavitation in wastewater treatment, by increasing the rate of reaction between calcium hydroxide and phosphates to improve wastewater treatment and phosphate removal [9]. A manual hydrodynamic cavitation water treatment device based on the same theoretical principles has been patented [10]. Save et al. investigated in the biotechnology sector facing the large scale microbial cell disruption of yeast cells [11].

In relation to the biodiesel production the assistance of hydrodynamic cavitation is a promising approach. The transesterification reaction of vegetable oils using base catalyst and short-chain alcohols were studied in the presence of hydrodynamic cavitation by Gogate et al. [8]. With this technique it is possible to prepare alkyl esters from triglycerides at pilot plant-scale. It has been proven that the application of cavitation for the transesterification reaction can achieve more than 90% product yield [8]. In the work of Ji et al. [12], biodiesel was prepared through the transesterification of soybean oil with the help of power ultrasonic and hydrodynamic cavitation reactors. It was found that hydrodynamic cavitation had positive effects on the transesterification reaction [12]. An experimental setup based on hydrodynamic cavitation was created for the production of biodiesel blend of *Citrullus colocyntis* (Thumba) oil [13]. In 2011 Gordon et al. have field a patented application on a process for producing biodiesel through lower molecular weight alcohol-targeted cavitation with a mechanical device which provokes the formation of cavitation in a fluidic flow [14].

In contrast to the previous studies, the present investigations focus on the destructive effect of cavitation on the hydrocarbon chains of vegetable oils to bypass the transeterification process and enhance the biodiesel production.

In our experiments, we used two different designs to generate hydrodynamic cavitation. To prove the formation of cavitation it was helpful to utilize a model reaction: the decomposition of Potassium Iodide (KI). Possible effects on this reaction have already been analyzed [15,16] and successfully applied [9]. Afterwards, we replaced the potassium iodide with a solution of Corn Oil

and water. It was stirred with different settings adjusted by variations in stirring time and propeller rotations. The samples were analyzed with GC, GC-MS and NMR technique previous and after the experiments to compare the molecular structure.

2. MATERIALS AND METHODS

The first experimental setup to generate cavitation consisted of a PS1501S DC Compact Power Supply (0-15 V, 0-1 A), a 400 ml VWR® Griffin Low Form beaker and a small propeller. An Extech Laser Tachometer was used to indicate the number of rotations generated by the propeller. A larger experimental design was constructed for the second test series. It consisted of a 5 gallon holding tank which was connected by two hoses with a Pacific Hydrostar Portable Utility Pump (120 V~, 60 Hz, 8,4 A, Flow: 1500 GPH, 25 GPM, 3500 RPM). To one side of the holding tank a supply line was connected to the pump. From the pump a second line supplied the suspension back into the holding tank. The formation of the cavitation was provoked by slots (length: 20 mm, width: 3 mm, depth: 2 mm) sliced into the front housing of the propeller blades. As a pre-step for the oil analyses a test series with Potassium Iodide (KI) solution was performed to prove the formation of cavitation. The decomposition of potassium iodide liberating iodine which provokes a change in the absorbency is subject to this pre-step. [16,9]. Therefore, it was possible to ensure that the Vegetable Oil, which was stirred in the identical apparatus, will be affected by cavitation. To obtain the model reaction, 0.5 M Potassium Iodide solutions were prepared with tap water. The absorbency was measured by the use of a Hach DR 1900b portable spectrometer at 355 nm previous, during, and after the cavitation experiment. The solutions differ in the number of rotations comprised by the propeller and the pump. In the smaller experiment setup one solution was stirred at 4000 RPM and the second one at 6000 RPM for 15 minutes. Six liter of the 0.5 mol/L solution was pumped in the bigger experiment setup for the same time.

The rise in absorbency due to the liberation of iodine caused by the formation of hydrodynamic cavitation was considered as a confirmation to keep the experiment design for the vegetable oil.

The Corn Oil was chosen for further experiments and therefore stirred with the presence of water.

Two water-oil solutions with different ratios were prepared. The first one consisted of 20% corn oil and 80% water and was processed with the propeller speed of 4000 RPM. The second one consisted of 5% corn oil and 95% water and was pumped in the bigger experiment setup. Both samples were analyzed five to six days after the experiment. This retention time was necessary for the emerging phase interface to prevent possible water residuals in the samples. Those water injections could provoke back flashes in the GC affecting the results adversely.

Sample were analyzed with a gas chromatograph model Shimadzu GC-2010 (Column: RTX-Biodiesel TG w Guard Column, Film thickness: 0.10 µm, Column length: 12.0 m, Inner diameter: 0.32 mm, Maximal temperature: 385°C, Initial temperature: 50°C, Rate: 10 °C/min, End temperature: 350°C, Carrier gas: Helium) before and after the cavitation experiments due to the fact that GC has been the most common method for the analyses of biodiesel. It is in that way possible to quantify even minor components [17]. To identify the mass of the components and to clarify the rise of new peaks, the Perkin Elmer - Clarus 580 Gas Chromatograph coupled to a Clarus SQ8S Mass Spectrometer (Column: Velocity-5 with 5% Diphenyl and 95% Dimethyl Polysiloxane, Film thickness: 0.25 µm, Column length: 30.0 m, Inner diameter: 0.3 mm, Initial temperature: 60°C, Rate: 10°C/min, End temperature: 330°C) was used. This was followed by analyses with the Bruker 600 MHz NMR Advance III using a 5 mm BBOF prodigy cold probe.

3. RESULTS AND DISCUSSION

The results of the absorbency measurements caused by the liberation of iodine during the experiment is shown in Fig. 2. They plot the amount of absorbency versus the time of the measurements. Two test series with a potassium iodide solution of 0.5 mol/l at 4000 rpm and 6000 rpm Fig. 2, were prepared in each case for both rotation settings in the small experiment setup. An upward trend can be noticed in both figures. The 6000 RPM setting shows the sharpest increase in the first five minutes. After that, the absorbency rises with a decreasing slope. The rapid rise happens after five minutes compared to the 4000 RPM setting. At this configuration the absorbency reaches the highest amount of 1.214 Abs.
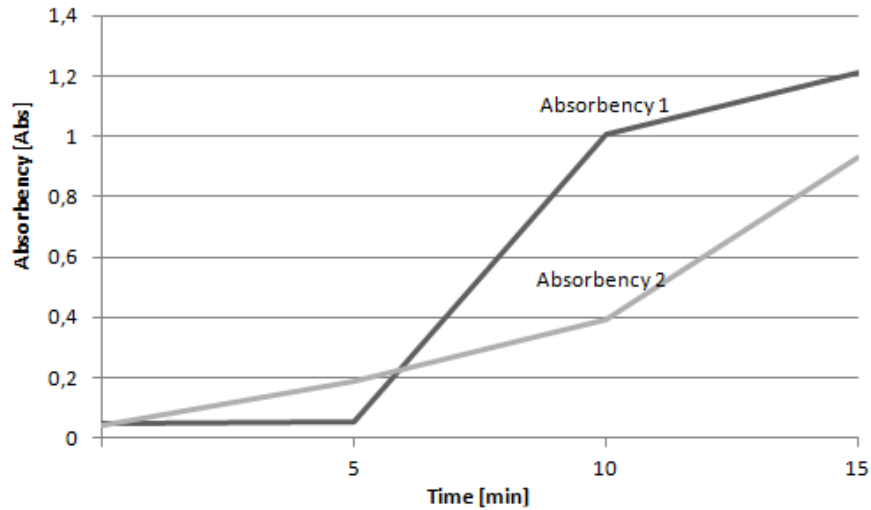
4000 RPM, 15 min

Fig. 1. Development of Absorbency, 0.5 mol/L Potassium Iodide solution, small experiment setup
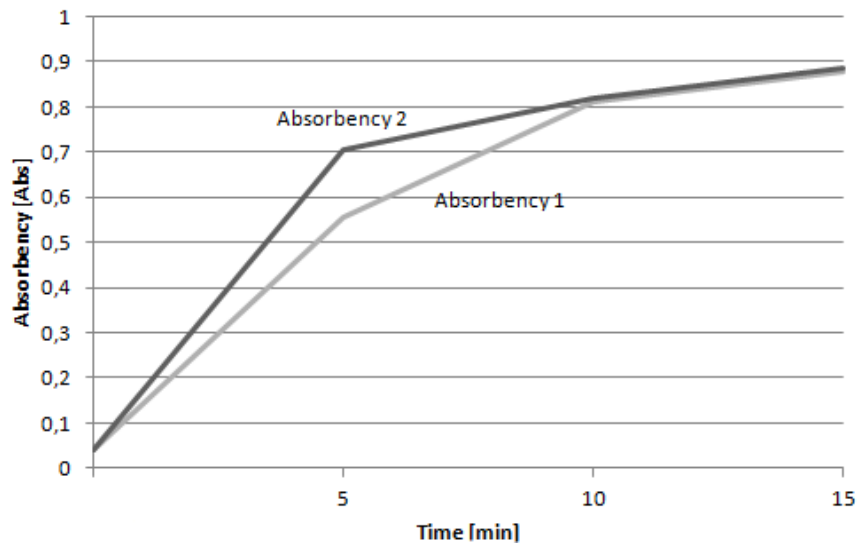
6000 RPM, 15 min

Fig. 2. Development of absorbency, 0.5 mol/L Potassium Iodide solution, small experiment setup

Four test series were run in the bigger experiment setup. Fig. 3 shows that the initial Absorbency rises due to the fact that the same solution was used four times with a 24 hour retention time between them. This lead to a slight decrease of absorbency before every test run. In comparison to the figures above, the slope of all graphs is lower due to the fact that the rotations per minute generated by the pump does not reach the amount of the small experiment setup. Another reason could be that the volume of the potassium iodide solution was much higher because the bucket had a load capacity of 5 gallons. To ensure a moderate occupancy rate,

six liters of KI solution were pumped during the experiment. This is about 15 times higher than the stirred amount of solution in the first experiment setup. Along with lower rotations per minute the liberation of iodine takes longer and rises slower. During the second test run one single decrease of Absorbency shows in the last five minutes. The liberated iodine in this solution is not uniformly distributed. This could appear as a decrease, but intensities of cavitation can differ in different areas of the solution [18]. For the reason that the other three test runs represent an increase, the observed decrease for Absorbency 2 test at 10 min. in Fig. 1 can be neglected. In summary, as evident from the graphs, both test rigs are proven to be appropriate to apply hydrodynamic cavitation on liquids.
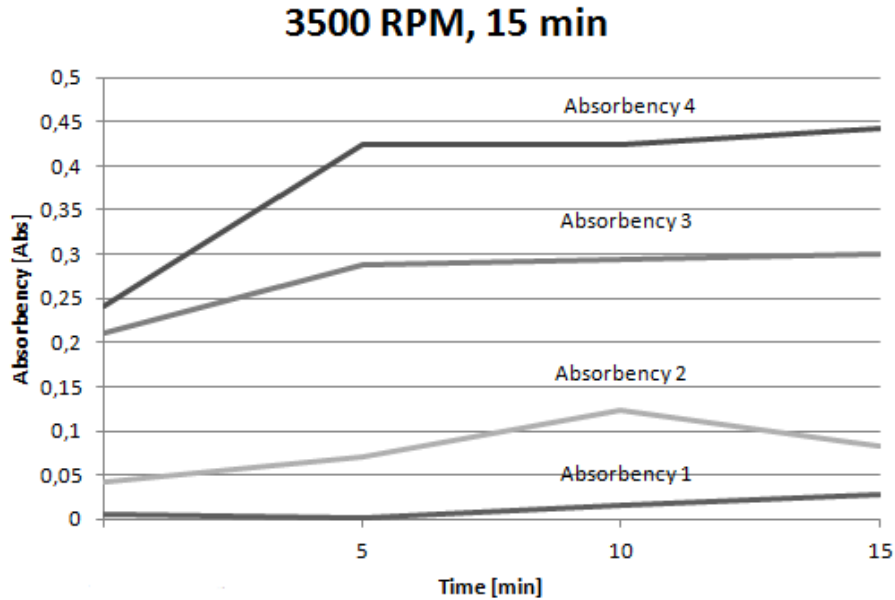

Fig. 3. Development of absorbency, 0.5 mol/L Potassium Iodide solution, big experiment setup
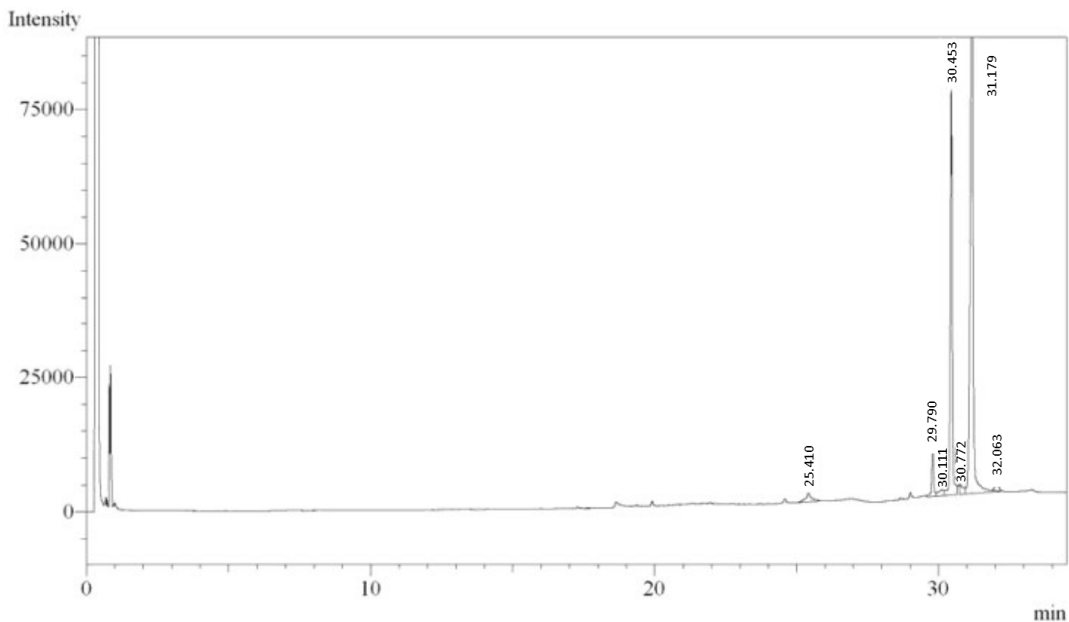

Fig. 4. Original corn oil GC analyses

The analyses of the corn oil samples with the GC prior Fig. 4 and after cavitation Fig. 5 showed the formation of new peaks between 10 to 25 minutes of retention time. To clarify this phenomenon the GC-MS analyses were used. The related spectra are shown in Fig. 6 and Fig. 7. Those peaks could not be identified using this method as an automatic matching with the database resulted in the typical spectrum of Octasiloxane. Siloxanes are common contaminants in the GC-MS technique and mostly derive from septum bleed [19]. It occurs when volatile materials of the septum, brought up to operating temperature, reach the column. For the reason that these contaminants affected the results of the analyses, the samples were analyzed with the NMR technique.
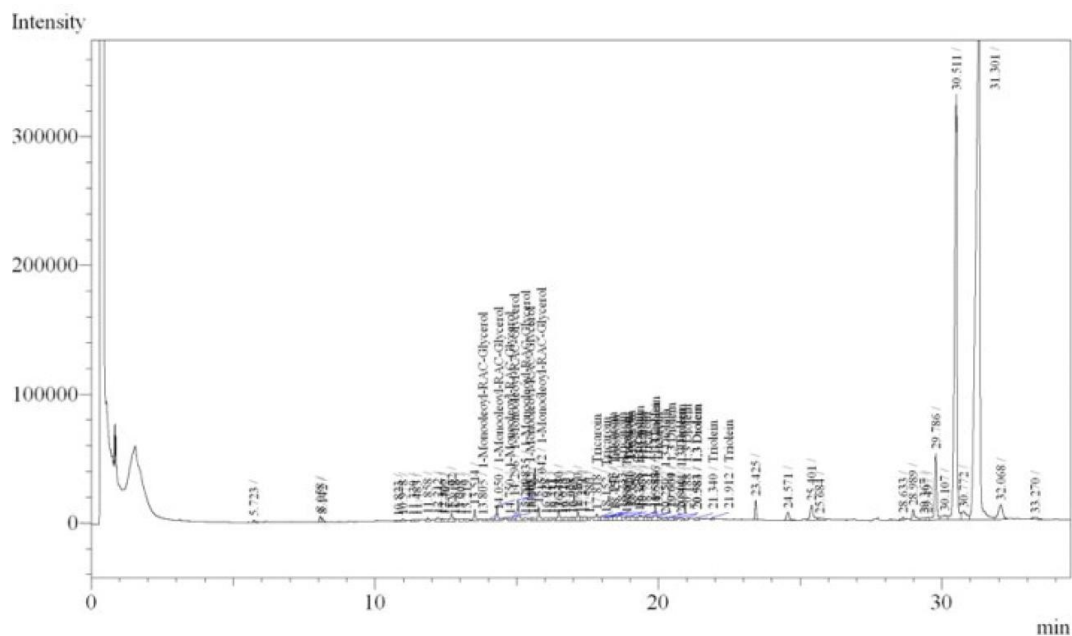
Peak#	Ret.Time	Area	Height	Conc.
1	5.723	10315	1878	0.000
2	8.058	19322	4822	0.000
3	8.142	14869	3245	0.000
4	10.823	11757	1056	0.000
5	10.978	16118	1822	0.000
6	11.330	11012	1256	0.000
7	11.483	11990	1383	0.000
8	11.858	19454	2582	0.000
9	12.212	26188	2520	0.000
10	12.366	10202	1957	0.000
11	12.462	15639	1904	0.000
12	12.702	34006	6256	0.000
13	12.818	10266	2078	0.000
14	13.008	15271	1765	0.000
15	13.219	17035	1665	0.000
16	13.514	50895	9232	0.000
17	13.805	15290	1651	0.000
18	14.050	24313	1663	0.000
19	14.296	49965	12110	0.000
20	14.402	15817	2049	0.000
21	14.750	13537	2008	0.000
22	14.835	17857	1987	0.000
23	15.042	80018	16475	0.000
24	15.299	20952	2307	0.000
25	15.505	11309	2195	0.000
26	15.576	16634	2075	0.000

Fig. 5. Corn oil GC analyses, cavitation with propeller at 4000 rpm, 15 min
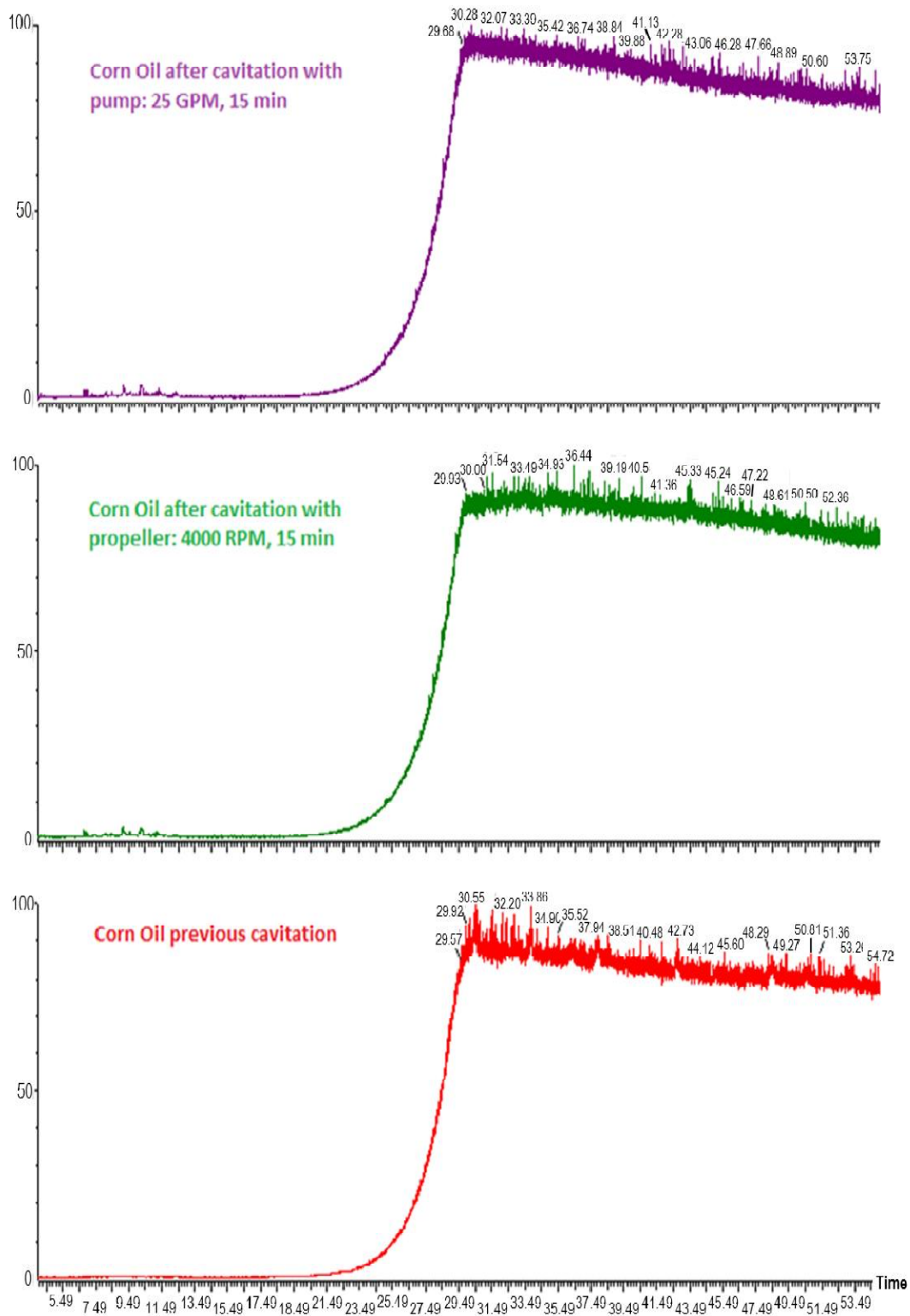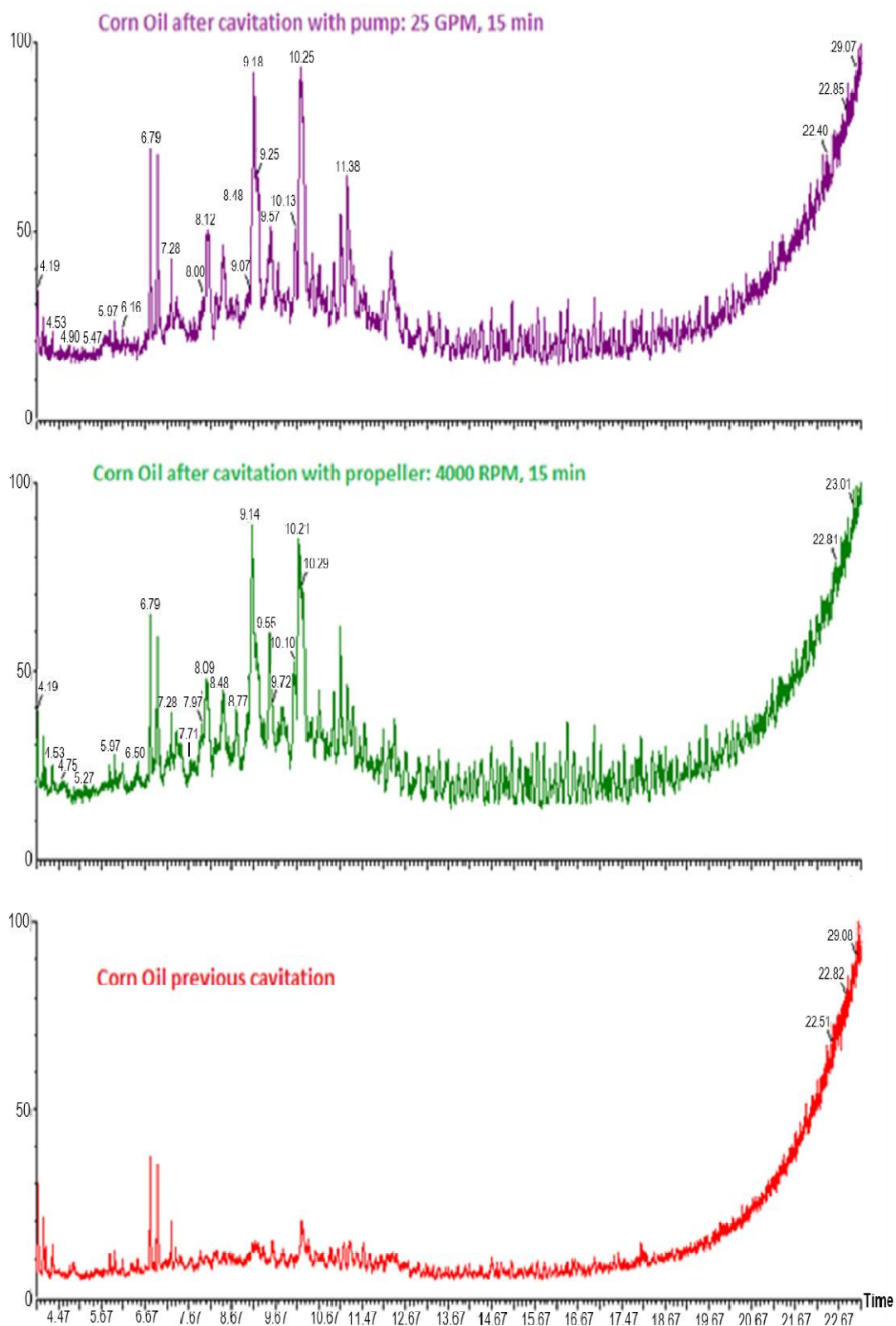
Fig. 6. GC-MS analyses

Fig. 7. GC-MS analyses, area of new peaks

By the use of the Bruker 600 MHz NMR it was possible to generate a closer look into the molecular structure of the oils. The spectra of the samples displayed a similar structure with four new peaks in comparison to the original oil as shown in Fig. 8 and Fig. 9. From the sample of the experiment with the propeller, two broad signals at 8.03 ppm and 7.98 ppm, and two peaks at 6.58 ppm and 6.02 ppm as shown in. The sample from the experiment with the pump also showed two broad signals at 7.98 ppm and 7.91 ppm with two peaks at 6.59 ppm and 6.02 ppm as shown in Fig 9. Although the cavitation has been applied with different devices, the curve characteristics differ only slightly. It indicates that the origin of the hydrodynamic cavitation created by two different experiment designs has a similar impact on the oil. All of the peaks are located in the typical chemical shift area of olefins [20]. It suggests that the influence of cavitation has provoked a destructive effect. The formation of new peaks implies the creation of new molecules. The ratio of the integrated olefin peak areas allowed the determination of how much olefin was generated in each experiment. The Olefin peaks of the propeller sample between 5.21 ppm and 6.6 ppm and the peak at 6.58 ppm have been integrated and normalized to 100%. It results in 0.313% of new olefin formation versus 99.687% already existing olefin content of the starting oil (Fig. 10). The same approach was repeated for the pump sample (Fig. 11). A similar ratio of new Olefin formation and starting oil was observed. To sum up, it was possible to provoke a formation of new molecules which indicates destruction on the hydrocarbon chains on a low level.
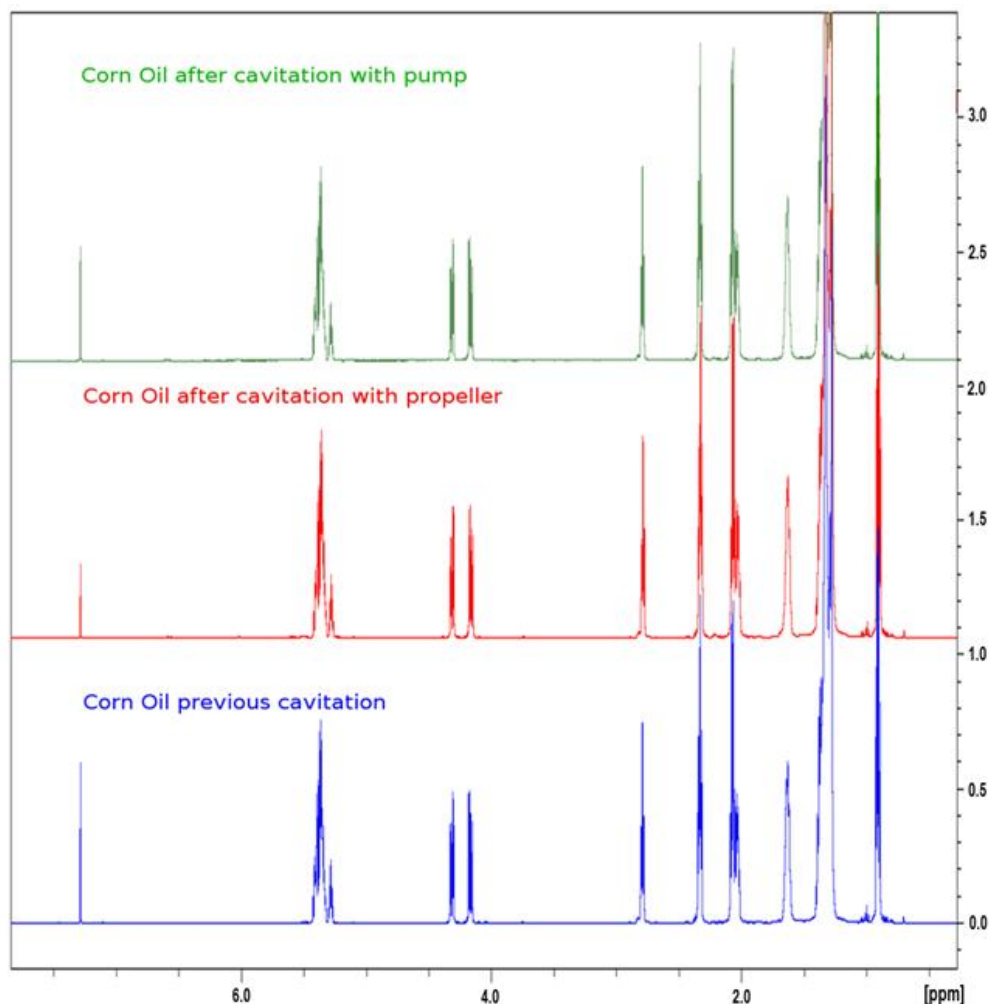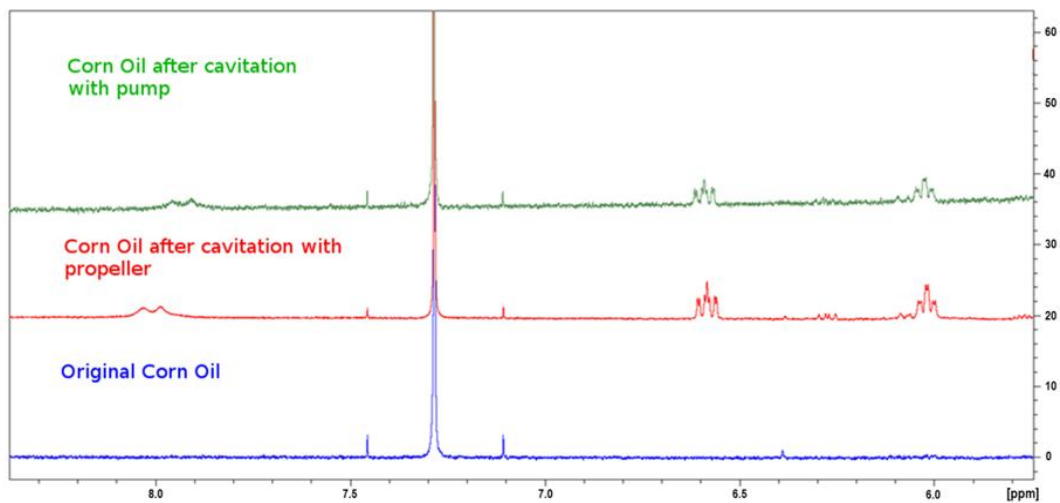

Fig. 8. NMR analyses
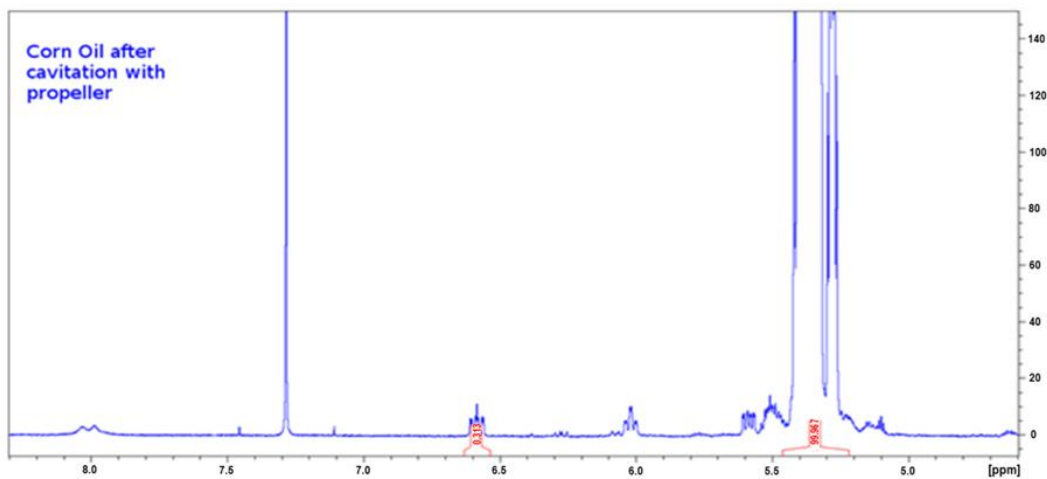
Fig. 9. NMR analyses, area of new peaks

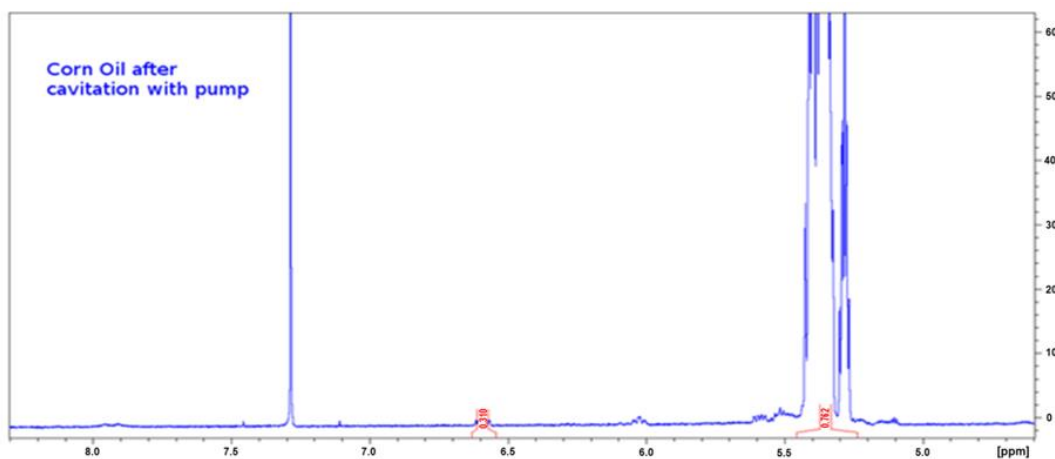**Fig. 10. Olefin yield of propeller experiment**

Fig. 11. Olefin yield of pump experiment

4. CONCLUSION

This paper investigated the destructive effect of hydrodynamic cavitation on corn oil hydrocarbon chains.

By the use of a model reaction, the decomposition of Potassium Iodide (KI), it was possible to prove the ability of the two experiment designs to generate cavitation. This was the requirement for further experiments with the Corn Oil in the identical setups. GC analysis of the results was influenced by septum bleed which was confirmed through GC-MS technique. It indicated that this technique was not the suitable for the analyses of the Corn Oil samples. Investigations with NMR analyses succeeded with a greater resolution which facilitated a detailed insight into the chemical structure of the oil. In that way, the formation of new peaks or new molecules could be discovered. Some new signals were detected and localized in the typical chemical shift areas of olefins. This observation indicates some modification of hydrocarbon chains. The areas of these peaks were very small relative to the peak areas corresponding to the starting oil. This is a limited extent of hydrocarbon cracking and far too little to bypass the transesterification reaction in the biodiesel production. It was therefore not possible to generate biodiesel. Based on the mentioned results it is likely that specialized hydrodynamic cavitation devices could achieve greater destructive effects. Further studies could focus on the improvement of the experiment setups.

ACKNOWLEDGEMENTS

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Demirbaş A. Biodiesel: A realistic fuel alternative for diesel engines. London: Springer. 2008;56:133.
2. Giannelos PN, Zannikos F, Stournas S, Lois E, Anastopoulos G. Tobacco seed oil as an alternative diesel fuel: Physical and chemical properties. Industrial Crops and Products. 2002;16(1):1-9.
3. Demirbaş A. Biodiesel fuels from vegetable oils via catalytic and non-catalytic supercritical alcohol transesterifications and other methods: A survey. Energy Conversion and Management. 2003;44: 2093-2109.
4. Fangrui M, Hanna MA. Biodiesel production: A review. Bioresource Technology. 1999;70(1):1-15.
5. Lusas EW. Animal and vegetable fats, oils and waxes. In: Kent JA. Handbook of Industrial Chemistry and Biotechnology, New York: Springer. 2012;1323-1402.
6. Singh D, Bhoi R, Ganesh A, Mahajani SM. Synthesis of biodiesel from vegetable oil using supported metal oxide catalysts. Energy & Fuels. 2014;28(4):2743-2753.
7. Michel JR, FC, Kozyuk O. Hydrodynamic cavitation processing. In: Letcher T., Scott J., Patterson D.: Chemical Processes for a Sustainable Future, Cambridge: Royal Society of Chemistry. 2014; Chapter 5.
8. Gogate PR, Tayal RK, Pandit AB. Cavitation: A technology on the horizon. Current Science. 2006;91(1):35-46.
9. Von Bargen MR. Hydrodynamic cavitation of calcium hydroxide and wastewater for phosphorus reduction and removal. Master Thesis, State University of New York: College of Environmental Science and Forestry, Syracuse, New York; 2016.
10. McGuire D (Inventor), Ecosphere Technologies, Inc. (Assignee). Manual hydrodynamic cavitation treatment device. United States Patent US 2014/0202942 A1, July 2014.
11. Save SS, Pandit AB, Joshi JB. Scale microbial cell disruption. IchemE. 1997; 75(C):41-49.
12. Ji J, Wang J, Li Y, Yu Y, Xu Z. Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation. ScienceDirect, Ultrasonics. 2006;44:e411-e414.
13. Pal A., Verma A, Kachhwaha SS, Maji S. Biodiesel production through hydrodynamic cavitation and performance testing. Renewable Energy. 2010;35:619-624.
14. Gordon R, Gorodnitsky I, Grichko V. Cavitation Technologies, Inc. (Assignee). Process for producing biodiesel through lower molecular weight alcohol-targeted cavitation. United States Patent Application US 2011/0151524 A1, June 2011.
15. Senthil Kumar P, Siva Kumar M, Pandit AB. Experimental quantification of chemical effects of hydrodynamc cavitation. Chemical Engineering Science. 2000;55:1633-1639.

16. Vichare NP, Gogate PR, Pandit AB. Optimization of hydrodynamic cavitation using a model reaction. Chemical Engineering Technology. 2000;23(8):683-690.

17. Knothe G, Van Gerpen J, Krahl J. The biodiesel handbook. Illinois, AOCS Press. 2005;(72).

18. Gogate PR, Manickam S, Pandit A. Cavitation reactors: Efficiency assessment using a model reaction. AIChE Journal, 2001;47(11):2526-2538.

19. Smith ED, Sorrells KE. A quantitative comparison of gas chromatograph septum bleed. Journal of Chromatographic Science. 1970;(9):15-17.

20. Zerbe O, Jurt S. Applied NMR spectroscopy for chemists and life scientists. Weinheim, WILEY-VCH. 2014; (35).

Peer-review history:
The peer review history for this paper can be accessed here:
http://sciencedomain.org/review-history/18718