

Catalytic Cracking of Vegetable Oils for Producing Biofuel

Ferial Zaher¹, M.S.Gad², Saadia M. Aly¹, S. F. Hamed¹, Ghada A. Abo-Elwafa¹, H. A. Zahran¹

¹Fats and Oils Department, Food Industry and Nutrition Division, ²Mechanical Engineering Department, Engineering Research Division, National Research Centre, 33 EL Bohouth st., Dokki, Giza, Egypt, P.O.12622.

CASTOR oil as well as used cooking oil have been catalytically cracked using three types of catalysts being zinc chloride, sodium carbonate and calcium oxide and the products of cracking were tested for their chemical and physical properties relevant to their use as fuels. Products obtained by cracking castor oil were found to be more suitable as bio-kerosene while those obtained by catalytic cracking of used cooking oil were more suitable as biodiesel. Therefore, the product obtained by catalytic cracking of used cooking oil has been then tested for its effect on the performance of a diesel engine compared to regular diesel fuel. Blends of catalytically cracked used cooking oil with regular diesel fuel were used for running the engine at different engine loading and the specific fuel consumption as well as the exhaust temperature had been determined at each load. The results have shown that blending of regular diesel fuel with catalytically cracked oil resulted in a reduction in the thermal efficiency compared to that if the engine was run using regular diesel fuel only .Such blending resulted also an increase in the exhaust temperature.

Keywords: Biofuel, Biodiesel ,Bio-kerosene ,Diesel engine, Vegetable oils.

The replacement of fossil fuels by other alternative fuels which are more sustainable and more friendly to the environment continues to be of a major concern by the whole world [1,2]. This is greatly attributed to two major problems facing the world .The first problem is the gradual and rapid reduction in natural petroleum resources with expectation of their depletion in the very near future. Such reduction in natural petroleum resources is due to the continuous increase of the energy consumption rate. Energy consumption increases due to the increase in world population as well as the rate of energy consumption per capita. The second problem is the global warming which is attributed to the excessive emission of carbon dioxide as the rate of fossil fuel consumption increases. Plant oils are considered the major candidate as a feedstock for the production of such alternative fuels yielding what is commonly

Corresponding author email: mgad27@yahoo.com, *Telephone: +202 0122295756.

Doi: 10.21608/ejchem.2017.2967

© 2017 The National Information & Documentation Center (NIDOC)

referred to as biofuels [3,4]. However, the high viscosity of plant oils compared to regular petrol fuels constitutes a major problem when used for running an engine due to their poor atomization. Improper fuel atomization leads to incomplete combustion with subsequent formation of carbon deposits on the injector tip of the diesel engine [3-6]. Therefore, plant oils should be treated either chemically or physically to reduce their viscosities prior to their use as fuels. Physical means for the reduction of oil viscosity include its blending with regular petrol fuels or blending with short chain alcohols in presence of a suitable surfactant such as 1-octanol [3]. On the other hand, chemical modification of plant oils to reduce their viscosity can be made either by trans-esterification of the oil with short chain alcohols [3-6] or by their catalytic cracking to short chain hydrocarbons [4,7]. Trans-esterification of plant oils yields products of a molecular weight almost one third that of the original oil with subsequent reduction in oil viscosity. Trans-esterification of vegetable oils with short chain alcohol can be made using alkaline or acidic catalysts. In general, alkaline catalysts are more effective than acidic catalysts. However, acidic catalysts are rather preferred when the oil acidity is high such as the case with used cooking oils. Non catalyzed trans-esterification of plant oils can be also achieved successfully if the process is carried out at the supercritical conditions of the alcohol used [8-10]. In fact, the composition of the fuel product obtained by trans-esterification is dependent on the type of feedstock used rather than the process conditions. The reverse is true if the oil is catalytically cracked whereby the product can be greatly controlled by controlling the process variables including the cracking temperature as well as the type of catalyst used. The production of biodiesel by direct esterification of fatty acids with short chain alcohols occurs in one step only whereby acidic catalysts can be used to speed up the reaction [11-13].

In Egypt, there is a great shortage in edible oils so that almost 90% of the consumption needs are currently imported. Therefore, it is not advisable to use edible oils for the commercial production of biofuel. Non edible oils that can be used are either castor oil or used cooking oil which became no longer suitable for edible purposes.

The present work has been initiated to assess the potential of both types of the previously mentioned feedstock for the production of biofuel. The catalytic cracking technology will be used since the product quality can be controlled via controlling the cracking conditions.

Materials and methods

Two types of non-edible oils commonly available in Egypt have been used in this study being castor oil and used cooking oil collected from local restaurants in Cairo city in Egypt. Both types of oils have been catalytically cracked whereby they were heated in a rounded bottom one liter flask mounted in a heating mantle and connected to a condenser and a receiving unit. The temperature of the oil was gradually raised to 450°C in presence of a catalyst and

the decomposition products were distilled off, condensed and collected in a receiving unit until completed. Three catalysts have been used for cracking being calcium oxide, sodium carbonate and zinc chloride and the weight of the catalyst was 3% of the oil weight. The cracking products were then evaluated for their fuel properties as compared to regular diesel fuel using ASTM methods [14]. They have been determined in the central analytical lab at the Egyptian Petroleum Research Institute, EPRI, Nasr City, Cairo following the standard methods of analysis (ASTM). These include the calorific value (ASTM D-224), Flash point (ASTM D-93), carbon residue (ASTM D-189), ash% (ASTM D-482), sulfur% (ASTM D-4294), pour point (ASTM D-9), kinematic viscosity (ASTM D-445) and density (ASTM D-4052). The product of catalytic cracking of used cooking oil was found to have properties closer to regular diesel fuel and therefore it was chosen for the engine performance test compared to regular diesel.

Experimental

The tested engine was Deutz made, single cylinder, four stroke, water cooled, direct injection, F1L511 model diesel engine. Its specifications are given in Table 1. This engine was connected to an eddy current dynamometer to measure the engine speed and load. The engine was equipped to measure fuel consumption, engine speed and exhaust gas temperature. This engine received air through an air box fitted with an orifice for measuring air consumption. A pressure differential meter was used to measure the pressure difference between the two sides of the orifice. Fuel consumption rate was measured using a glass burette and stop watch. Tested engine speed was measured using a digital tachometer. The schematic diagram of experimental set up is shown in Fig.1. The engine was warmed up before taking all readings. The measurements were recorded after the engine reached its stable condition. The engine was operated with regular diesel fuel (D100), catalytically cracked oil (B100) and blends of both of them. The volumetric percentage of catalytically cracked oil in these blends was 20, 40, 60 and 80% (B20, B40, B60 and B80), respectively. The engine speed was maintained constant at rated speed of 1500 rpm and the performance parameters were studied such as specific fuel consumption, thermal efficiency, exhaust gas temperature, volumetric efficiency and air- fuel ratio.

TABLE 1. Test Engine specifications.

Engine parameters	Specifications
Type	Deutz
Model	F1L511
Number of cylinders	Single
Cycle	Four stroke
Cooling	Air
Cylinder diameter (mm)	100
Piston stroke (mm)	105
Compression ratio	17:1
Rated speed	1500 rpm
Maximum output power	7.7 hp

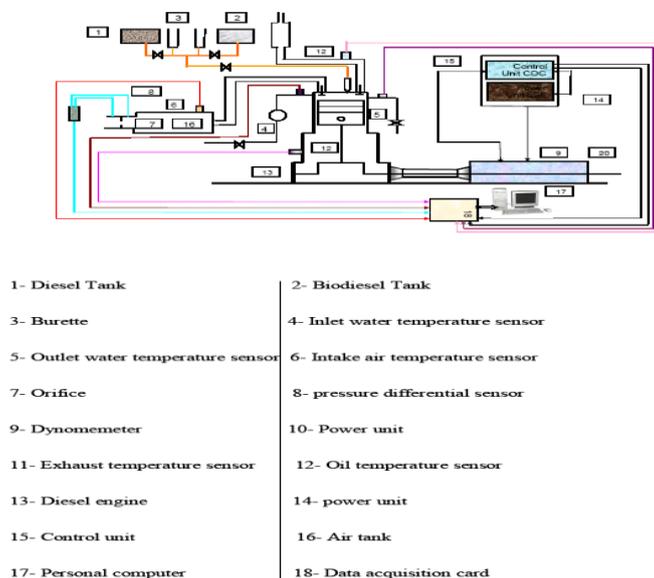


Fig. 1. Schematic Diagram of diesel Engine test rig burning diesel and catalytically cracked vegetable oils.

Results and Discussions

Properties of thermally cracked castor oil and used cooking oil

Tables 2 and 3 list the fuel properties of catalytically cracked products using castor oil and used cooking oil, respectively as compared to standard Egyptian specifications of diesel fuel. These include the density, ash %, kinematic viscosity, carbon residue sulfur %, pour point, flash point and calorific value. It is obvious that the viscosity of all the cracked products were a little high as compared to that of regular diesel fuel. It is expected therefore that its atomization in the engine will be worse than that of diesel oil. This may result in a reduction in the combustion efficiency in the combustion chamber with subsequent problems of formation of carbon deposits. However, these products are advantageous over diesel oil since they are completely free of sulfur. Sulfur oxidation during fuel combustion releases corrosive oxides which have an adverse impact on the environment and the engine components as well. The products obtained by catalytic cracking of castor oil are characterized by having low flash points which make them less safe during handling and storage. Moreover, their calorific values are lower than that of regular diesel fuel with expectation of less output power upon their combustion. However, their pour points are extremely low suggesting their possible use as bio-kerosene rather than biodiesel.

On the other hand, the products obtained by catalytic cracking of used cooking oil have properties closer to those of regular diesel fuel with higher calorific values which prove its potential as an alternative fuel to regular diesel fuel. Therefore these cracked products have been assessed for their effect on the performance of a diesel engine running using these products as a fuel.

TABLE 2. Fuel properties of products of catalytic cracking of castor oil using 3% calcium oxide, sodium carbonate and zinc chloride as catalysts ; B1, B2 and B3 respectively compared to standard Egyptian specifications of diesel fuel.

Property	Method	B1	B2	B3	Diesel fuel
Density @ 15.56°C	ASTM D-4052	0.88	0.86	0.87	0.82-0.87
Ash content, wt%	ASTM D-482	Nil	Nil	Nil	≤ 0.01
Kinematic viscosity, cSt, @ 40°C	ASTM D-445	6.45	6.20	5.8	≤ 7
Total sulfur, wt. %	ASTM D-4294	Nil	Nil	Nil	≤ 1.2
Carbon residue, wt. %	ASTM D-189	Nil	0.41	Nil	≤ 0.1
Flash point, °C	ASTM D-93	39	39	38	≥ 55
Pour point, °C	ASTM D-97	-30	-36	-39	4.5-15
Calorific value, kJ / kg	ASTM D-224	34190	34924	37000	42000

TABLE 3. Physical and chemical properties of catalytically cracked used cooking oil using 3% sodium carbonate and calcium oxide as catalysts.

Property	Method	Sodium Carbonate	calcium oxide	Diesel fuel
Density @ 15.56°C	ASTM D-4052	0.8761	0.8765	0.82-0.87
Ash content, wt. %	ASTM D-482	0.03	Nil	≤ 0.01
Kinematic viscosity, cSt, @ 40°C	ASTM D-445	6.45	6.20	≤ 7
Total sulfur, wt. %	ASTM D-4294	Nil	Nil	≤ 1.2
Carbon residue, wt. %	ASTM D-189	Nil	Nil	≤ 0.1
Flash point, °C	ASTM D-93	73	90	≥ 55
Pour point, °C	ASTM D-97	9	12	4.5-15
Calorific value, kJ / kg	ASTM D-224	42339	42359	42000

Effect of catalytically cracked used cooking oil and its blends with diesel fuel on engine performance

Figures 2-6 show the effects of engine load as well as the percentage of catalytically cracked oil in its blends with regular diesel fuel on the specific fuel consumption, thermal efficiency, exhaust gas temperature, air-fuel ratio and

volumetric efficiency. In these figures, D100 and B100 refer to pure regular diesel fuel and pure catalytically cracked oil respectively. B20, B40, B60 and B80 refer to fuel blends containing 20, 40, 60 and 80% by volume of catalytic cracked oil, respectively.

It is clear from Fig. 2 that specific fuel consumption gradually decreases by increasing the engine load and also by decreasing the percentage of the cracked oil. At full engine load, specific fuel consumption using pure regular diesel fuel was 0.28 kg/kW.hr compared to 0.38 kg/kW.hr if catalytically cracked oil has been used for engine running. Increase in specific fuel consumption when catalytically cracked oil is used for diesel engine running instead of regular diesel oil occurs although both oils have almost same calorific value as listed in Table 3. This indicates that the combustion of catalytically cracked oil in diesel engine occurs less efficiently than that of regular diesel fuel. Inefficient combustion usually occurs due to poor fuel atomization in the engine in case of viscous fuels. The viscosity of catalytically cracked used cooking oil is in general a little high compared to what is recommended in regular diesel fuel as listed in Table 3.

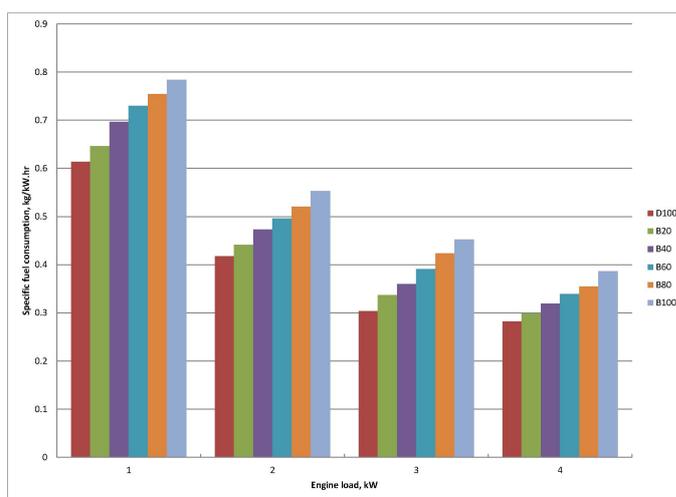


Fig. 2. Effect of engine load and percentage of catalytically cracked used cooking oil in its blend with diesel fuel on specific fuel consumption.

Thermal efficiency using the fuel blends previously mentioned have been estimated on the basis of specific fuel consumption and heating value of each blend. As shown in Fig. 3, the thermal efficiency was found to gradually decrease by increasing the percentage of thermally cracked oil in the fuel blend. At full engine load, the thermal efficiency using catalytically cracked oil (B100) was 18% lower than that using regular diesel fuel (D100). However, it has been

reported in a recent study that thermal efficiency can be improved by 12% by blending regular diesel fuel with an equal volume of biodiesel prepared by transesterification of used cooking oil with methanol [15].

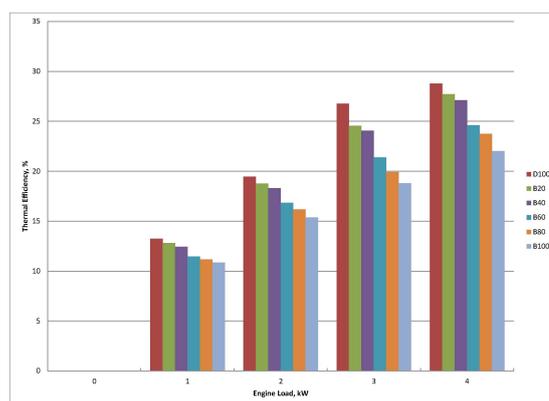


Fig. 3. Effect of engine load and percentage of catalytically cracked used cooking oil in its blend with diesel fuel on the thermal efficiency.

The effect of blending regular diesel fuel with catalytically cracked oil on exhaust gas temperature is illustrated in Fig.4. It is obvious that exhaust gas temperature has been increased regularly by increasing the percentage of catalytically cracked oil in the blend. The exhaust temperature was 225 °C using regular diesel fuel, D100 compared to 265°C using pure catalytically cracked oil (B100) indicating a marked increase of heat lost in the exhaust. This result is quite expected since the increase in the percentage of catalytically cracked oil in the fuel blend effects an increase in the specific fuel consumption which was also accompanied by a reduction in the thermal efficiency.

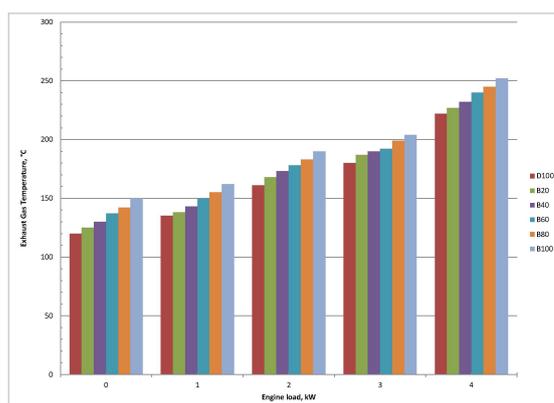


Fig. 4. Effect of engine load and percentage of catalytically cracked used cooking oil in its blend with diesel fuel on the exhaust temperature.

Figures 5 and 6 showed the effect of blending regular diesel fuel with catalytically cracked oil on the air-fuel ratio and volumetric efficiency, respectively. It can be seen that both of the two parameters gradually decreases with increasing the engine load as well as the percentage of catalytically cracked oil in the fuel blend. At full engine load, the use of catalytically cracked oil instead of regular diesel fuel for engine running resulted in a reduction in air-fuel ratio and volumetric efficiency by about 33% and 4%, respectively.

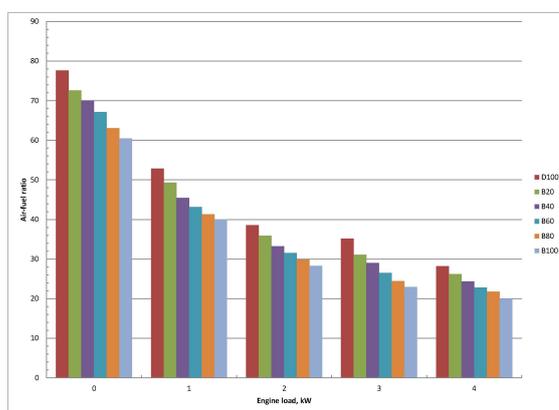


Fig. 5. Effect of engine load and percentage of catalytically cracked used cooking oil in its blend with diesel fuel on the air-fuel ratio.

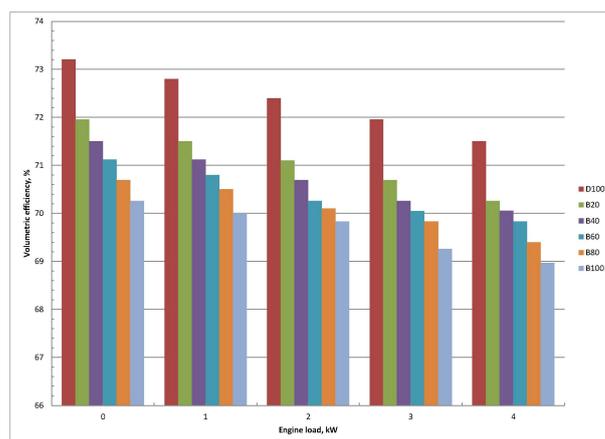


Fig. 6. Effect of engine load and percentage of catalytically cracked used cooking oil in its blend with diesel fuel on the volumetric ratio.

Conclusions

It can be concluded that:

- Environmentally friendly Fuels alternative to petroleum fuel can be produced by catalytic cracking of plant oils.
- Catalytic cracking of highly viscous plant oils; castor oil, would yield products more suitable as bio-kerosene rather than biodiesel while the reverse is true if regular used cooking oil is catalytically cracked.
- Running a diesel engine using thermally cracked oil or their blends with regular diesel fuel would result in a reduction in the thermal efficiency as well as an increase in the temperature of the combustion exhaust as compared to regular diesel fuel.

References

1. **Bender, M.**, Potential conservation of biomass in the production of synthetic organics, *Resources conservation and recycling*, **30**, 49-58 (2000).
2. **Demirbas, M.F.**, Current technologies for biomass conversion into chemicals and fuels, *Energy Sources*, Part A **28**, 1181-8 (2006).
3. **Zaher, F.A.**, Vegetable Oils as Alternative Fuel for Diesel Engines, *Grasas, Y. Aceites*, **41**, pp. 82-91 (1990).
4. **Megahed, O.A.**, Utilization of Ricebran Oil for the Production of Diesel Engine Fuel, *Ph.D. Thesis*, Cairo University (1996).
5. **Zaher, F.A., Megahed, O.A. and El Kinawy, O.S.**, Esters of sunflower oil as an alternative fuel for diesel engine, *Energy sources*, **25**, 1015-1022 (2003).
6. **Zaher, F.A., Megahed, O.A., Abdallah, R.I and Nabil, D.** Rapeseed oil esters as diesel engine fuel, *Energy Sources*, **26**, 119-126 (2004).
7. **Zaher, F.A., El-Noamany, H.M., Megahed, O.A. and Abdallah, R.I.**, Catalyzed Thermal Cracking of Rice bran Oil to Produce Bio-fuel, *Middle East J. of Applied Sciences*, **(5)**, 274-280 (2015).
8. **Demirbas, A.**, Biodiesel from vegetable oils via transesterification in supercritical methanol, *Energy Conversion and Management*, **43**, 2349-2356 (2002).
9. **Hawash, S., Kamal, N., Zaher, F.A., Kinawy, O.S. and El Diwani, G.**, Biodiesel Fuel from Jatropha Oil Via Non - Catalytic Supercritical Methanol transesterification, *Fuel*, **88**, 579-582 (2009).
10. **Kusidiana, D. and Saka, S.**, Kinetics of esterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol, *Fuel*, **80**, 693-698 (2001).

11. **El-Kinawy, O.S. and Zaher, F.A.**, Studies on Esterification Kinetics of Short Chain Alcohols With Fatty Acids to Produce Biodiesel Fuel, *Energy Sources*, part A, **34**, 662-670 (2012).
12. **El-Galad, M.I., El-Khatib, K.M. and Zaher, F.A.**, Economic Feasibility Study of Biodiesel Production By Direct Esterification of Fatty Acids From the Oil and Soap Industrial Sector, *Egyptian J. of Petroleum*, **24**, 455-460 (2015).
13. **Zaher, F.A. and Soliman, H.M.**, Biodiesel Production by Direct Esterification of Fatty Acids With Propyl and Butyl Alcohols, *Egyptian J. of Petroleum*, **24**, 439-443 (2015).
14. **ASTM**, Annual Book of Standards Petroleum Products and Lubricants, section 5, Vol. (5.01-5.03), American Society of Testing and Materials, Philadelphia, USA (1995).
15. **Zaher, F. and Gad, M.S.**, Assessment of biodiesel derived from waste cooking oil as an alternative fuel for diesel engines, *International J. of Chem. Tech. Research*, Vol. 9 (3), 140-146 (2016).

(Received 19/12/2016;

Accepted 23/1/2017)

التكسير الحفزي للزيوت النباتية لإنتاج الوقود الحيوي

فريال عباس زاهر¹، محمد صابر جاد²، سعاد مصطفى على¹، سعيد فتوح

حامد¹، غاده أبو الوفا¹، حمدي عبد الهادي زهران¹

¹ قسم الدهون والزيوت- شعبه الصناعات الغذائية والتغذية، ² قسم الهندسة الميكانيكية- شعبه البحوث الهندسية- المركز القومي للبحوث- 33 شارع البحوث، الدقي، الجيزة، مصر، رقم بريدي 12622.

قد تم تكسير زيت الخروع وكذلك زيت الطهي المستعمل حفزيا باستخدام ثلاثة أنواع من المحفزات وهي كلوريد الزنك وكربونات الصوديوم وأكسيد الكالسيوم وتم اختبار الخصائص الكيميائية والفيزيائية لنواتج التكسير التي يمكن استخدامها كوقود. وقد وجد من نواتج تكسير زيت الخروع أنه يمكن استخدامه ككبروسين حيوي في حين وجد من نواتج التكسير الحفزي لزيت الطهي المستعمل أنه يمكن استخدامه كديزل حيوي. ناتج التكسير الحفزي لزيت الطهي المستعمل تم اختبار تأثيره على أداء محرك الديزل مقارنة بوقود الديزل العادي. تم خلط مزيج من زيت الطهي المستعمل التي تم تكسيه حفزيا مع وقود الديزل العاد لتشغيل المحرك عند ظروف تحميل مختلفه، كما تم قياس الاستهلاك النوعي للوقود وكذلك درجة حرارة العادم عند كل حمل للمحرك. وأظهرت النتائج أن خلط وقود الديزل العاد مع الزيت الذي تم تكسيه حفزيا أدى إلى انخفاض الكفاءة الحرارية للمحرك بالمقارنة بتشغيل المحرك باستخدام وقود الديزل العادي فقط. هذا الخليط أدى أيضا إلى زيادة درجة حرارة العادم.