

USE OF CITRIC ACID ESTERS AS ALTERNATIVE FUEL FOR DIESEL ENGINES

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ABSTRACT: Common fuels for (adapted) diesel engines are fossil diesel fuel, fatty acid methyl ester (FAME or biodiesel) or vegetable oils. Further potential biogenic substitutes are the citric acid esters tributylcitrate (TBC) and triethylcitrate (TEC). Their use as fuel was applied for a patent in Germany in 2010. Proposed advantages are low soot combustion, independence of energy imports due to the possibility of local production and a broad raw material base. Comparison of their properties with relevant fuel standards showed, that only some of the demands are met. However, few rapeseed oil characteristics (e. g. oxidation stability and viscosity) can be improved if the citric acid esters are used as a blend component. The operating and emission behaviour of a vegetable oil compatible CHP unit fuelled with various rapeseed oil/TBC blends were investigated and a trouble free and soot emission reduced engine operation due to the high molecularly bound oxygen content was observed. Long term test runs are necessary for an entire technical validation.

Keywords: citric acid ester, fuel, biofuel, diesel

1 INTRODUCTION

Due to the limited availability of fossil resources and the dramatically increase in fuel prices, biogenic alternatives are gaining more and more importance. Furthermore, a better greenhouse gas balance is expected for certain biofuels compared to fossil fuel and due to their chemical properties also lower values for specific limited exhaust components have been observed.

Two potential alternatives for fossil diesel fuel are the citric acid esters triethylcitrate (TEC) and tributylcitrate (TBC). Their use as fuel was applied for patent in Germany in 2010 (DE 10 2009 015 441 A1). According to the patent applicant the advantages are low soot combustion, independence of energy imports due to the possibility of local production and a broad raw material base. Until now no scientific examinations of the citric acid esters concerning their fuel properties and emission behaviour have been conducted and no use as fuel in large scale is known [6].

2 OBJECTIVE

It was the purpose to examine the chemical properties of the citric acid esters and to assess their suitability as fuel. In a further step various dosed admixtures to diesel and rapeseed oil fuel should be investigated concerning their influence on fuel quality. At last test runs of a CHP unit fuelled with the respective blends should be conducted.

3 STATE OF THE ART

Triethylcitrate and tributylcitrate are esters of citric acid and ethanol or 1-butanol (Fig. 1 and Fig. 2). Nowadays citric acid is industrially produced by fermentation of carbohydrates by means of a transgenic type of the mold fungus *Aspergillus niger*. Also the alcohols can be produced by fermenting carbohydrates, butanol via the bacteria *Clostridium acetobutylicum* and ethanol via yeast e.g. *Saccharomyces cerevisiae* or the bacteria *Zymomonas mobilis*. Due to the fact that lignocellulose can be converted in fermentable carbohydrates, not only sugar or starch from grain or beets are possible feedstock for the production of citric

acid esters but also waste wood or straw. In a further step the respective alcohol and the carbon acid are finally bonded by a three step esterification. Current fields of application are use as plasticizers in the plastics industry, food additive or pharmaceutical [9][1][10][4].

Triethylcitrate has an oxygen content of 40.4 wt-% and tributylcitrate of 30.7 wt-% [4]. It is known that oxygenated fuels or mixtures of oxygenated fuels and oxygen-free fossil fuels are causing lower soot emissions when burned in engines. Different studies have proven that fuels with oxygen contents of more than 38 wt-% or for example an admixture of 30 vol-% E85 to diesel fuel enable a nearly soot free engine operation [7][8].

Due to the high oxygen content of the citric acid esters advantages in the soot emission behaviour were expected and were already determined qualitatively by the patent applicant but not according to standardised methods. Fuel relevant parameters such as ignitability, lubricity or viscosity have been widely unknown.

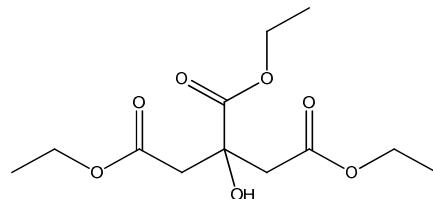


Figure 1: Triethylcitrat (TEC) ($C_{12}H_{20}O_7$)

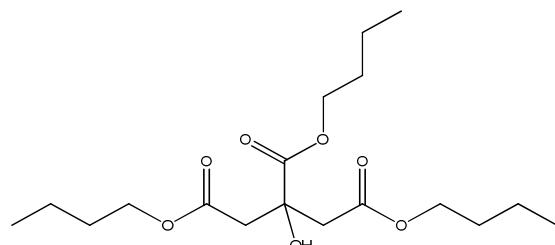


Figure 2: Tributylcitrat (TBC) ($C_{18}H_{32}O_7$)

In Germany, both citric acid esters are grouped in water hazard class 1, which is defined as slightly

hazardous to water [2]. Rapeseed oil fuel is not hazardous to water. That means that a maximum content of 2.9 wt-% of TBC or TEC is allowed to be added to rapeseed oil fuel if the mixture should remain not hazardous to water according to the rules for classifying mixtures (annex 4 VwVwS). Diesel fuel is hazardous to water, water hazard class 2 [2].

4 MATERIALS AND METHODS

In order to evaluate the characteristics and the suitability of triethylcitrate and tributylcitrate as fuel for diesel engines, HOFENEDER [4] investigated both fuels by laboratory analysis regarding 22 fuel relevant parameters. Afterwards the results have been compared with the demands of the standards for diesel fuel (DF) (DIN EN 590), rapeseed oil fuel (RF) (DIN 51605) and FAME (DIN EN 14214). An excerpt of the most important values is shown in **Table I**.

Furthermore the characteristics of various mixtures of the citric acid esters and diesel fuel respectively rapeseed oil fuel have been analysed concerning heating value, oxidation stability, dynamic viscosity and ignition delay.

In the last step HUBER [5] investigated mixtures of TBC and rapeseed oil as fuel in a vegetable oil compatible combined heat and power unit (CHP). The system was equipped with all necessary measurement devices in order to evaluate the operating and emission behaviour. The CHP was operated at about 90 % load (7.3 kW electrical power output) with all different fuels. The TBC content was increased step by step in following concentrations: 2.9; 10; 20; 30; 40 and 50 wt-%. All mentioned emission and operating values are mean values of three 30 minute averages. Dust load of the exhaust gas has been determined according to the standard VDI 2066. The limited gaseous emissions hydrocarbon (HC), carbon monoxide (CO) and nitrogen oxides (NO_x) have been continuously measured by a gas analysis system. The TBC content was increased in steps until the emission optimum was reached. Tests with TEC mixtures have not been conducted due to the insufficient miscibility with diesel and rapeseed oil fuel.

5 RESULTS

5.1 Laboratory analysis of the pure esters

Element content (ICP-Screening)

For TEC the concentrations of undesirable elements (Na, K, Mg, Ca, P) have been within the specification of the mentioned fuel standards and have been in the range of the detection limit of 0.5 mg/kg. For TBC the sodium (45 mg/kg) and phosphor (10 mg/kg) content exceeded the limits of both biofuel standards considerably. A reason for that could be found in the production process, where amongst others sodic supplies are used [4]. Deposits at the injection valves or a reduced service life of an exhaust gas aftertreatment system have to be expected when an engine is operated with a fuel with such high Na and P contents.

Derived cetane number (ignition delay)

The ignition delays of the citric acid esters were measured with a Fuel Ignition Tester and the results have been converted into a derived cetane number with an empiric formula. The values were found to be 18.4 for TEC and 25.4 for TBC and are therefore below the minimum demand of 40 for rapeseed oil fuel. Poor cold-start behaviour of an engine operated with pure citric acid esters is assumed [4].

Distillation range

The requirements of the diesel fuel standard concerning the distillation range of both TEC and TBC were met [4]. The vaporisation of the citric acid esters occurs in a diesel engine conform temperature range

Density

The density at 15 °C of TEC is 1145 kg/m³ and of TBC it is 1046 kg/m³. The limits of all three standards are considerably exceeded by both substances [4]. As the initial jet spreading or spray angle decreases with decreasing gas/liquid density ratio, the fuel/air mixing in the cylinder is negatively influenced by a fuel with higher density [3].

Flash point

The flash point of TEC is 171 °C and of TBC 125 °C. The requirements of DIN EN 590 (55 °C), DIN 51605 and DIN EN 14214 (both 101 °C) are met [4]. No additional safety requirements regarding fire prevention in storage and transport compared to the standard fuels are necessary.

Net calorific value

The minimum stipulated net calorific value for rapeseed oil fuel is 36 MJ/kg. The requirement is neither fulfilled by TEC (20 MJ/kg) nor by TBC (26 MJ/kg) [4]. Despite the higher density of the esters also the volume associated net calorific value is considerably lower than for DF and RF. A higher consumption and a lower cruising range of a so fuelled vehicle is the result.

Oxidation stability

The oxidation stability according to DIN EN 15751 of both citric acid esters is more than 100 hours. The requirements of all three standards are easily met. No excessive oxidation and polymerisation with resulting filter plugging have to be expected [4].

Acid number

The acid numbers of TEC and TBC are very low and the requirements of the standards are easily met. No increased wear and corrosion due to acid fuel components have to be presumed [4].

Lubricity

The lubricity of the citric acid esters was found to be very good and the requirements are met. No problems due to excessive wear have to be expected [4].

Kinematic Viscosity

The kinematic viscosity at 40 °C of TEC is 11.7 mm²/s and of TBC it is 12.5 mm²/s. Neither TEC nor TBC can fulfil the requirements of DIN EN 590 (max. 4.5 mm²/s) and DIN EN 14214 (max. 5 mm²/s). The limit of the rapeseed oil standard DIN 51605 of maximum 36 mm²/s is met by both esters [4]. Conveying characteristics and atomisation of the esters are expected to be better than of RF but worse than of DF and FAME.

Table I: Comparison of the fuel relevant properties of DF, FAME, RF, TEC and TBC [4]

Properties	DF Limit values DIN EN 590	FAME Limit values DIN EN 14214	RF Limit values DIN 51605	TEC Analysed values	TBC Analysed values
C-content in wt-%*	85.9	76.8	77.5	52.3	60.3
O-content in wt-%*	0	11.0	10.9	40.4	30.7
H-content in wt-%*	13.6	12.1	11.6	7.3	9.0
P-content in mg/kg	-	< 4.0	< 3.0	< 0.5	9.6
Na-content in mg/kg	-	(Na + K)	-	0.7	45.0
K-content in mg/kg	-	< 5.0	-	< 0.5	< 0.5
Ca-content in mg/kg	-	(Ca + Mg) < 5.0	< 1.0	< 0.5	< 0.5
Mg-content in mg/kg	-	-	< 1.0	< 0.5	< 0.5
S-content in mg/kg	< 10	< 10	< 10	6.8	14.2
Ash content in wt-%	< 0.01	< 0.02	-	< 0.005	< 0.005
Cetane number	> 51.0	> 51.0	-	-	-
Derived cetane number	-	-	> 40	18.4	25.4
Distillation range					
Vol-% at 250 °C	< 65	-	-	0	38
Vol-% at 350 °C	> 85	-	-	100	100
95 vol-% at temperature in °C	< 360	-	-	299	258
Density at 15 °C in kg/m ³	820.0 - 845.0	860.0 - 900.0	910.0 - 925.0	1144.8	1046.1
Flash point in °C	> 55	> 101	> 101	171.0	125.0
Total contamination in mg/kg	< 24	< 24	< 24	2	21
Net calorific value in MJ/kg	-	-	> 36.0	20.3	25.7
Carbon residue in wt-%	< 0.3	-	-	< 0.01	0.04
Copper strip corrosion [Corrosion class]	1	1	1	1	1
Oxidation stability in h	> 20	> 8.0	> 6.0	> 100	> 100
Acid number in mgKOH/g	-	< 0.50	< 2.0	0.01	0.02
Lubricity (wear scar diameter) in µm	< 460	-	-	224	255
Kinematic viscosity at 40 °C in mm ² /s	2.00 – 4.50	3.50 – 5.00	< 36.0	11.7	12.5
Water content in mg/kg	< 200	< 500	< 750	375	408
Water hazard class*	2	1	-	1	1

*) Property not included in any of the mentioned standards

5.2 Results of the laboratory analysis of mixtures of TEC/TBC with diesel or rapeseed oil fuel

Due to the polarity and the higher density of TEC, a phase separation was observed at mixtures with diesel and rapeseed oil fuel. TBC is less polar due to the higher alcohol butanol and is therefore readily soluble in diesel and rapeseed oil fuel.

As mentioned in chapter 5.1, the net calorific value of both citric acid esters is lower than that of DF and RF. With increasing TBC and TEC content the net calorific value of the mixtures is decreasing linear, see **Figure 8**.

TEC and TBC are featuring very good oxidation stability beyond 100 hours. Therefore the oxidation stability of rapeseed oil fuel can be increased by adding citric acid esters.

The kinematic viscosity of TEC and TBC is between RF and DF. Therefore the viscosity of DF is negatively influenced and that of RF is positively influenced by mixing it with a citric acid ester.

Pure TBC has an ignition delay of about 8 ms at 525 °C and 34 bar in a Fuel-Ignition-Tester (FIT). The value for pure RF is about 2.6 ms. The ignition delay in the FIT is defined as the time between the start of injection and the first pressure rise of 0.2 bar in the combustion chamber. **Figure 3** shows the values for different mixtures. It is obvious that the negative influence of the citric acid ester is low at minor dosage. Only at 80 wt-% TBC and 20 wt-% RF the ignition delay is doubled. For TBC and DF mixtures a similar behaviour was observed.

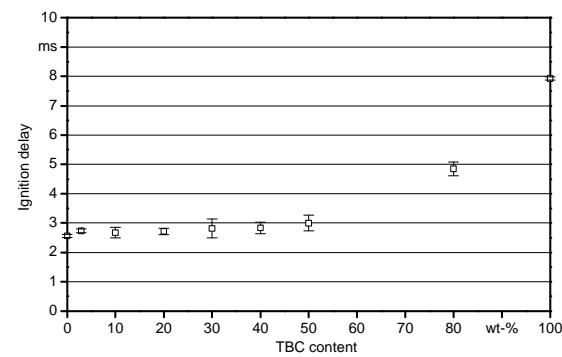


Figure 3: Ignition delay of rapeseed oil fuel and tributylcitrate mixtures, determined in a Fuel-Ignition-Tester (FIT).

5.3 Emission behaviour of the CHP unit fuelled with TBC – rapeseed oil fuel blends

By adding tributylcitrate to rapeseed oil fuel the dust emission behaviour of the CHP was significantly improved, see **Figure 4**. An optimum was detected between 30 and 40 wt-% TBC. Compared to pure RF a decrease of 40 % was achieved and compared to DF the dust emission have been halved. At 50 wt-% the dust emission increased again and the test series was stopped. As main reason for the initial improvement in soot formation an increasing oxygen content of the fuel was identified. Due to the decreasing net calorific value, more fuel has to be injected with increasing TBC content. Furthermore, a slower heat release and pressure increase was detected for the TBC blends compared to DF or RF in the constant volume ignition delay tester. Both are leading to a longer combustion time and the soot oxidation is influenced negatively so that the emission increases again.

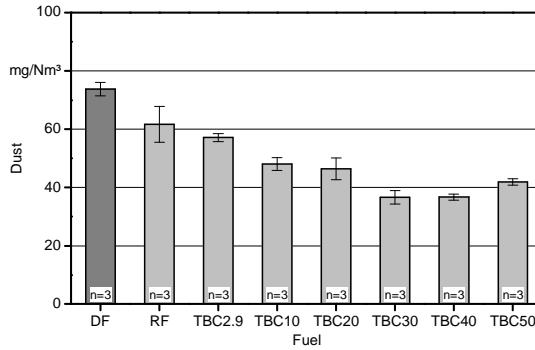


Figure 4: Dust emissions of the CHP unit operated with RF-TBC blends (e. g. TBC10 means rapeseed oil fuel with a content of 10 wt-% TBC etc.)

Carbon monoxide and hydrocarbon emissions are shown in **Figure 5** and **Figure 6**. They were hardly influenced by blending rapeseed oil fuel with tributylcitrate up to a concentration of 30 wt-%. At higher dosage the emissions were increasing significantly and even the DF value was clearly exceeded. Reason for that was similar to the dust emissions: An increasing combustion time was resulting in a more and more incomplete oxidation of CO and HC.

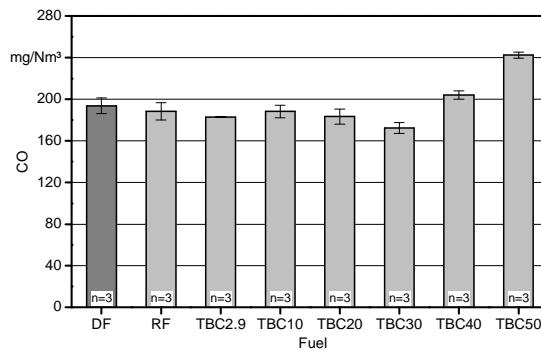


Figure 5: Carbon monoxide emissions of the CHP unit operated with TBC/RF blends

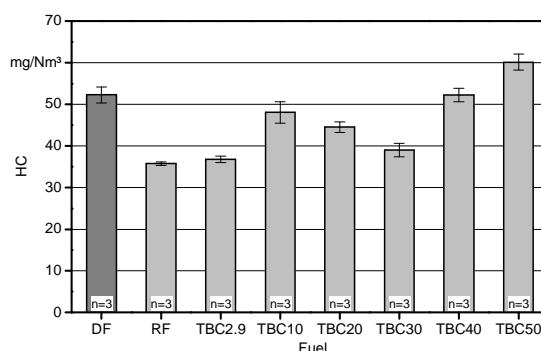


Figure 6: Hydrocarbon emissions of the CHP unit operated with TBC/RF blends

Admixture of TBC to RF did not lead to a dust/nitrogen oxide trade-off as often observed when measures are taken in order to reduce one of them. **Figure 7** shows that nitrogen oxides emissions were decreasing also with increasing TBC content. At 40 wt-% the emissions were falling even below the DF value.

Reason for that is the already mentioned slower pressure rise after the ignition and the shifting of the combustion towards late.

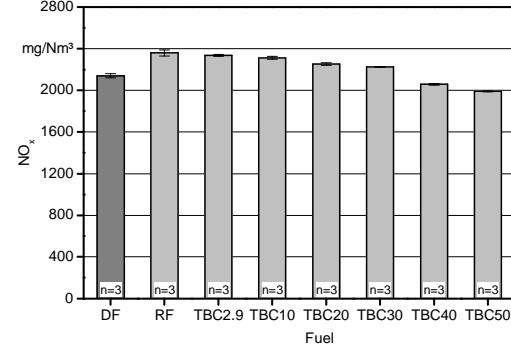


Figure 7: Nitrogen oxide emissions of the CHP unit operated with TBC/RF blends

5.4 Operating behaviour of the CHP unit fuelled with TBC – rapeseed oil fuel blends

During the short term studies a trouble free engine operation was assessed for all blends. The fuel consumption increased linear due to the decreasing net calorific value with rising TBC content, see **Figure 8**. Only at 50 wt-% the fuel consumption was disproportionately high. Reason for this is probably the more and more incomplete oxidation and utilization of the fuel.

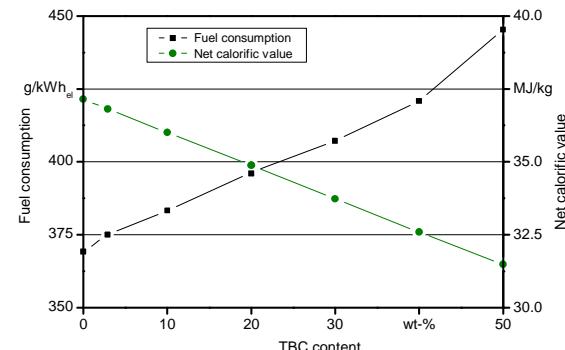


Figure 8: Net calorific value of TBC-RF blends and fuel consumption of the CHP

The efficiency of the CHP was hardly influenced by varying its fuel. The electrical efficiency for all pure fuels and blends was nearly constant at about 26 %, see **Figure 9**. Only for TBC50 the value was slightly lower, due to the same reasons as mentioned for the disproportional high consumption of this fuel. The overall efficiency for all different fuels was measured to be between 80 and 82%.

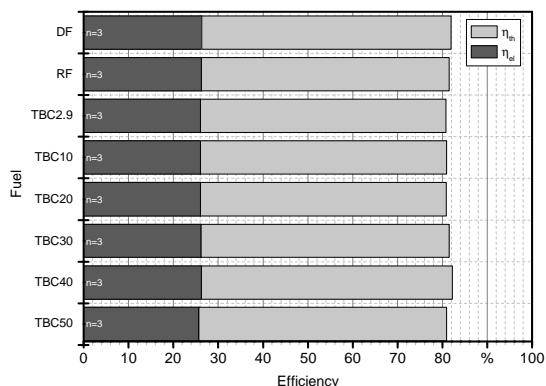


Figure 9: Electrical and thermal efficiency of the CHP unit with different fuels

6 CONCLUSION AND OUTLOOK

Due to the low ignitability of citric acid esters their use as a pure fuel for conventional diesel engines is problematic, but a limited admixture in order to improve the emission behaviour is possible. Test series with various fuel mixtures in a vegetable oil compatible CHP unit showed, that dust emissions could be reduced by 40 % by adding 30 wt-% of TBC to rapeseed oil fuel. Furthermore nitrogen oxides emissions could be reduced whereas carbon monoxide as well as hydrocarbon emissions remained at the same level. Due to the lower net calorific value of TBC, increased fuel consumption was observed. The engine efficiency however was hardly influenced. Further advantages of admixture of TBC to rapeseed oil fuel are improvements in viscosity and oxidation stability. The low ignitability of the citric acid esters is a disadvantage. Long term test runs are necessary for an entire technical validation.

7 REFERENCES

- [1] Arpe, H.-J. (2007): Industrielle Organische Chemie, Bedeutende Vor- und Zwischenprodukte, 6. vollständig überarbeitete Auflage. Weinheim: Wiley-VCH, 536 pages
- [2] Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit (2005): Allgemeine Verwaltungsvorschrift zur Änderung der Verwaltungsvorschrift wassergefährdende Stoffe vom 27. Juli 2005. Liste nicht wassergefährdender Stoffe gemäß Nummer 1.2a (Anhang 1); Liste wassergefährdende Stoffe, Stoffgruppen und Gemische gemäß Nummer 2.1.1 (Anhang 2), Bundesanzeiger, Jg. 57, Nr. 142a vom 30. Juli 2005, 36 pages
- [3] Heywood, J. B. (1988): Internal Combustion Engine Fundamentals. McGraw-Hill Series in Mechanical Engineering. New York: McGraw-Hill, 930 pages
- [4] Hofeneder, M. T. (2012): Eigenschaften und Eignung von Triethylcitrat und Tributylcitrat als Kraftstoff. Diplomarbeit. Durchgeführt am Technologie- und Förderzentrum im Kompetenzzentrum für Nachwachsende Rohstoffe. Hochschule Weihenstephan-Triesdorf, University of Applied Sciences. Weihenstephan-Triesdorf, 111 pages
- [5] Huber, G (2012): Emissions- und Betriebsverhalten eines Blockheizkraftwerks beim Einsatz biogener Kraftstoffe – Aufbau eines BHKW-Versuchsstandes und Messungen. Masterarbeit. Durchgeführt am Technologie- und Förderzentrum im Kompetenzzentrum für Nachwachsende Rohstoffe. Technische Universität München, 102 pages
- [6] Ingendoh, A., März, U. (2010): Zitronensäureester als Kraft- und Heizstoffe, Offenlegungsschrift, DE 10 2009 015 441 A1. Berlin: Deutsches Patentamt, 7 pages
- [7] Janssen, A.; Jakob, M.; Schnorbus, T.; Kolbeck, A. (2011): Chancen und Herausforderungen der Ethanolbeimischung zum Dieselmotorkraftstoff. MTZ Motortechnische Zeitschrift, Jg. 72, Nr. 7-8, S. 572–577
- [8] Janssen, A.; Muether, M.; Pischinger, S.; Kolbeck, A.; Lampert, M. (2009): Tailor-Made Fuels: The Potential of Oxygen Content in Fuels for Advanced Diesel Combustion Systems. SAE 2009 Fuels and Lubricants Meeting, San Antonio; 2009-01-2765
- [9] Kalschmitt, M.; Hartmann, H.; Baumbach, G.; Edelmann, W.; Good, J.; Hofbauer, H.; Lewandowski, I.; Meier, D.; Mory, A.; Nussbaumer, T.; Obernberger, I.; Remmeli, E.; Senn, T.; Spliethoff, H.; Stelzer, T.; Welling, J.; Widmann, B. (2009): Energie aus Biomasse - Grundlagen, Techniken und Verfahren. 2te Auflage. Berlin: Springer-Verlag, 1030 pages
- [10] Xu, J.; Jiang, J.; Wie, L. V.; Gao, Y. (2011): Synthesis of tributylcitrat using solid acid as a catalyst. Chemicel Engineering Communications, Band 198, Heft 4, pages 474-482



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