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Research Article

Catalytic Production of Liquid Fuels from Organic Residues of Rendering Plants

Anaerobic low temperature conversion (LTC) converts organic residues such as animal meal or meat and bone meal (MBM) to bio-crude, a solid product, containing carbon and phosphorus, reaction water and non-condensable gases. The yield of bio-crude increases with the content of volatile solids. The efficiency of the conversion as well as the calorific value of the liquid fuel produced are favorably affected by the partial recycling of inorganic constituents, high amounts of volatile solids and a low percentage of heteroatoms present in the feeding material. Heating values are 32.3 MJ/kg for bio-crude from animal meal and 19.5 MJ/kg for bio-crude from MBM. Both bio-crude and animal fat produced were effectively converted in a vertical reactor construction with a fixed bed of aluminosilicates of the zeolite family or acidic clays, respectively. Products are bio-fuels of varying chemical qualities. Depending on the reaction temperature and the catalyst type, aliphatic hydrocarbons (T = 400 °C, ~97 %) or alkylbenzenes (T = 550 °C) are the main products. The calorific values of these bio-fuels are in a range from 40.1 to 41.9 MJ/kg and the kinematic viscosities are between 0.9 and 2.29 mm^2/s. The solid products of LTC from different biomass (sludge, animal meal, MBM) contain a significant amount of phosphorus. In the case of the solid product from MBM it was as high as 242 mg P_2O_5/g. Solubility in citric acid showed that in the case of MBM, 98.8 % of total phosphorus is potentially available to plants. Pot experiments demonstrated a similar plant growth as with other organic fertilizers.

1 Introduction

As a result of the BSE (bovine spongiform encephalopathy) crisis, the disposal of about 0.7 million Mg of animal meal or meat and bone meal (MBM) from German rendering plants per year has become a problem [1]. Additionally 0.3 million Mg of animal fat are produced per year. By law, residues from rendering plants are excluded from animal forage. Therefore new options for utilization are required [2], in particular to the incineration of these wastes [3, 4]. One way is to convert animal residues including animal fat into liquid fuels [5], which would be in agreement with the European Community's aim to increase the portion of biogenic fuels up to 5.75 % until 2010 [6]. State of the art is the transformation of lipids into alkylesters analogous to the production of biodiesel from rapeseed, but the content of stearic acid in animal fat is a big problem. After alkylation, stearic acid alkylesters precipitate in the temperature range of 10 °C. This solubility behavior reduces the usability as a fuel in the motor pool of rendering plants.

Reduction of polarity is a key to this problem, which can be achieved by transformation into liquid hydrocarbons [7, 8]. This paper reports on laboratory results of the thermo-catalytic low temperature conversion (LTC) of organic residues from rendering plants to liquid hydrocarbons (bio-crude, bio-fuel).

2 Materials and Methods

2.1 Substrates and Catalysts

The applied organic residues used consisted of animal meal, MBM, and animal fat from a local rendering plant. Tab. 1 shows the analytical parameters of the biomass converted, indicating that the net calorific value as well as the carbon

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Table 1. Analytical parameters of different substrates used in LTC experiments.

|	Dry solids	Volatile solids (VS)	Bulk density	NCV	C	H	N	S
	[%]	[%]	[kg/m³]	[MJ/kg]	[%]	[%]	[%]	[%]
Animal meal	94.3	81.0	580	18.4	45.0	6.5	8.8	0.5
MBM	96.6	62.0	810	13.9	31.6	4.8	7.8	0.3
Animal fat	99.4	>99	–	37.0	76.2	12.1	N/D	N/D

content are increasing with the percentage of volatile solids. Under the reaction conditions, catalysts for conversion of animal meal or MBM to bio-crude are present in-situ in the form of inorganic trace element profiles of the corresponding substrates.

By contrast, when in-situ catalysts are missing, e.g. for upgrading of biomass-derived crude oil or for the direct conversion of animal fat to bio-fuel, external catalysts based on metal aluminosilicates [9] have to be applied.

Granular (2–5 mm) zeolite types such as shape selective ZSM-5, H-form (e.g. Pentasil, SiO_2/Al_2O_3 mole ratio = 50 ± 10) were examined. These zeolite catalysts were obtained from Chemie Uetikon, Switzerland. Wessalith is an Y-type zeolite (SiO_2/Al_2O_3 mole ratio = 100 ± 10) from Degussa, Germany.

2.2 Experimental Setup

The experimental system is schematically presented in Fig. 1. The thermocatalytic bench-scale unit consists of a Pyrex glass-tube (wall thickness 1 mm, inner diameter 70 mm, length 1400 mm) in a heat controlled block furnace (Heraeus/Kendro RO 10/100 R; rated power, 10.1 kW with a Controller RE 2.1). One end of the tube is connected to a nitrogen cylinder and the other end, a condenser, is attached to a gas trap and gas collection vessel In batch experiments, up to 1 kg of solid,
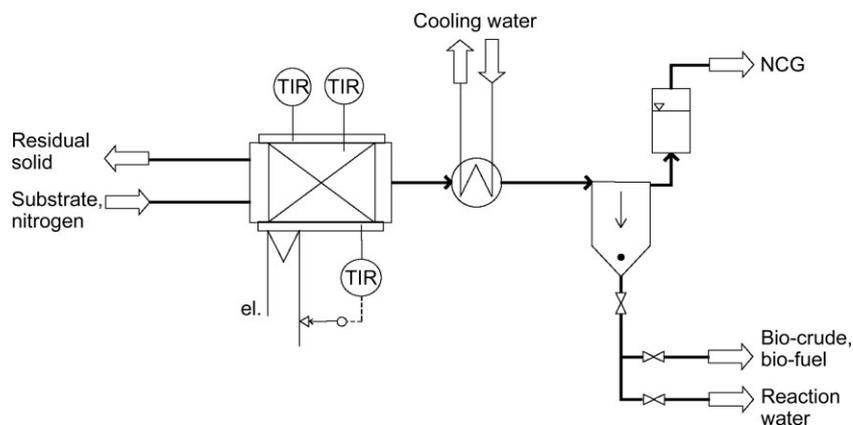
grinded biomass was filled into the glass tube, closed by glass wool stoppers and then heated up to the required temperature under the exclusion of oxygen. Emerging organic vapors as well as water steam are passing a water-cooled condenser, where the vapors are liquefied. The liquid products are collected in a separating funnel, whereas non-condensable gases are lead through the gas trap to the extractor hood.

For the conversion of animal fat or upgrading of biomass-derived bio-crude, a vertical reactor construction with a block furnace of Linn Higherm (Model FRHT-3-40/750/110) was used. The catalysts were fixed into a vertical quartz glass tube with an inner diameter of 29 mm and a length of 1100 mm located above a 1000 mL evaporation vessel of borosilicate. The height of the catalyst bed was 300 mm. This construction enforces the passage of the vapors through the fixed catalyst bed where catalytic reactions occur. Products are subsequently being liquefied in a following glass cooler. Non-condensable (C_1-C_3, H_2, CO_2) gases are led to the drain. Weight hour space velocities (WHSV) of 0.3–2.5 h^{-1} were applied. The temperatures within both the samples and the additional catalysts were determined by thermocouples Pt-100.

2.3 Analytical Methods

Prior to degradation studies, all substrates were routinely analyzed for C, H, N, S (Vario EL, Elementar Analysensysteme GmbH, Germany), dry matter, ash content (Furnace M 110, Heraeus, Germany) and calorific value (C7000 Calorimeter System, IKA, Germany). The fuel products obtained were analyzed by elemental analysis followed by infrared spectrometry (FT-IR Spektrum BX, Perkin Elmer, USA) with ATR unit (Pike Technology, USA), and nuclear magnetic resonance (NMR)-spectrometry (DRX 300, Bruker, Germany). Separation and identification of individual compounds were performed using a GC-MS (Varian, USA) under the following operational conditions: a CT-SPL 5CB wat fused silica column, 25 m × 0.3 mm; column temperature, 60 °C (10 min); 10 °C/min to 200 °C (90 min).

For the measurement of kinematic viscosities (v_T), Ubbelohde capillary viscosimeters (Schott, Germany) were applied. Thermogravimetric analysis (TG 209, Netzsch, Germany) was carried out using nitrogen gas with 20 mL/min and a heating rate of 10 °C/min. The phosphate content of residual solids was determined photometrically using test cuvettes (Dr. Lange, Germany). Phosphorus recovery rates were determined by the ratio of the percentage phosphate extractable by citric acid (2 %) and by aqua regia.

3 Results

The results from the thermo-gravimetric (TG) and differential weight loss thermogram (DTG) of MBM (see Fig. 2) exhibit two main weight loss regimes. The lower regime (80–150 °C) correlates with the
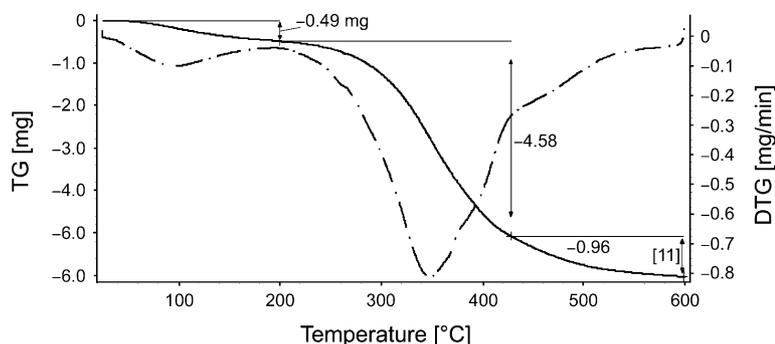

Figure 1. Scheme of the LTC plant on a laboratory scale.

Figure 2. Thermogravimetric diagram of meat & bone meal.
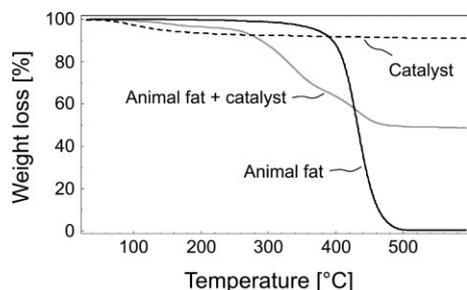

Figure 3. Thermogravimetric diagram of animal fat with and without acidic clay as an external catalyst.

evaporation of water while the upper regime (250–450 °C) is mainly due to the decomposition of carbohydrates, proteins and fats during the thermo-catalytic conversion. Based on this DTG data, the LTC-reactor temperature was set at 400 °C.

Considering Fig. 3, the diagram is restricted to the weight loss profile (TG). Without an external catalyst, the graph reflects the evaporation of animal fat with increasing temperature. In the presence of the zeolite catalyst Wessalith, the shape of the TG-curve varies between 250 and 50 °C , which indicates that chemical changes take place. The thermogravimetry of the catalyst alone shows no weight loss in this range.

3.1 Mass and Energy Yields

The percentage mass yields in relation to the mass of the organic residues fed was determined for the non-condensable gases (NCG), the bio-crude, water phase and solid product containing both inorganic solids as well as char (see Fig. 4). For a given feedstock, the yield of bio-crude increases with the organic carbon content [C] or volatile solids (VS), respectively (see Tab. 2). For example, laboratory scale LTC of animal meal ([C] = 45.0 %, [VS] = 81.0 %) gave rise to 29.2 % bio-crude, whereas the fuel yield from animal fat ([C] = 76.2 %, [VS] > 99 %) was 72.9 % in the case of a conversion temperature of 400 °C. In both cases, the production of oil started at approx. 280 °C. The energy balance of low temperature conversion of animal meal (see Fig. 5) (NCV = 18.8 MJ/kg) shows that 52.0 % of the energy could be conserved in bio-crude (NCV = 33.5 MJ/kg), whereas 32.7 % could be retrieved in residual solid (NCV = 14.4 MJ/kg).
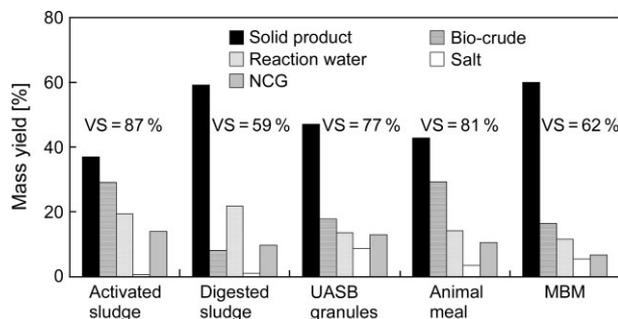

Figure 4. Mass yields for the LTC from different animal meal and MBM in comparison to the mass yield for the LTC from different sludges. (VS: Volatile Solids of Substrate).

3.2 Bio-crude/Bio-fuel

Figs. 5 and 6 illustrate the NMR-spectra of oils produced from both MBM as well as animal fat. ^{1}H-NMR of the bio-crude from MBM converted at 400 °C (see Fig. 6) showed that it consists of 97 % aliphatic ($\delta \approx 0.5$–2.4) and 3 % aromatic ($\delta \approx 7$) compounds. The limit value for polycyclic aromatic hydrocarbons (PAH) in Diesel is 10.5 % [10], whereas the content of PAH in GTL and CTL, respectively, is relatively low due to the complex production process of these fuels.

The results of ^{1}H-NMR could be confirmed both by ^{13}C-NMR and by ^{13}C-Dept NMR. In the Dept-mode, the CH_2 groups of the aliphatic hydrocarbons give characteristic intensive negative peaks at 20–40 ppm. These findings strongly suggest that the LTC bio-crude originates from the fatty acids in the lipids of the bio-mass.

The ^{1}H-NMR-spectrum of the bio-fuel produced by the conversion of animal fat in the presence of aluminosilicate at a reaction temperature of 400 °C is similar to that of the MBM.

However, bio-fuel from animal fat, converted at 550 °C with the ZSM-5 catalyst Pentasil, showed strong signals in the aro-
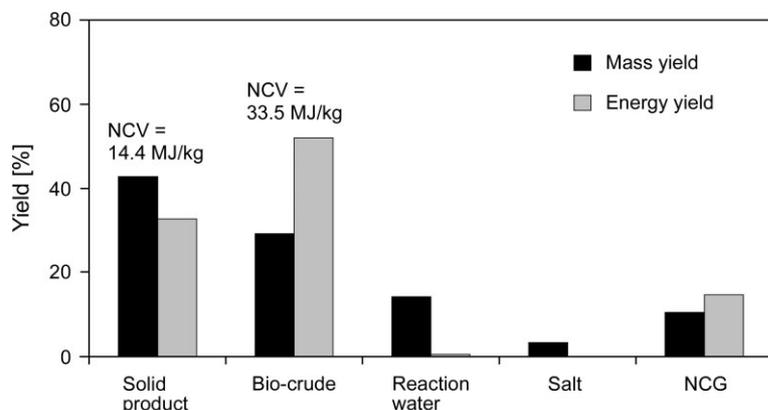
Table 2. Analytical parameters of bio-crude from MBM and bio-fuels from animal fat converted at 400 °C with the catalyst Wessalith and at 550 °C with the catalyst Pentasil.

	Yield	NCV	Density	$v_{40°C}$	C	H	N	S
	[%]	[MJ/kg]	[g/mL]	[mm²/s]	[%]	[%]	[%]	[%]
Animal meal	29.2	32.3	0.94	45.2	70.2	10.7	8.7	0.3
MBM	16.3	19.5	0.90	29.8	69.8	10.2	11.3	<0.34
Animal fat (400 °C)	72.9	41.9	0.80	2.29	86.1	13.8	<0.14	<0.34
Animal fat (550 °C)	31.5	40.1	0.84	0.74	88.6	10.7	<0.14	<0.34

Figure 5. Mass and energy yield for the LTC of animal meal.

matic region ($\delta \approx 7$) (see Fig. 7), which was confirmed by ^{13}C-NMR ($\delta \approx 120$–130). Separation and identification by GC-MS showed alkylbenzenes such as toluene, isomeric xylenes, mesitylene and isomeric trimethylbenzenes as prevailing compounds.

The corresponding infrared spectra (FTIR) are presented in Fig. 8 and 9. Bio-crude from the thermocatalytic conversion of animal meal shows broad bands centered around 3.350 cm^{-1} due to the hydrogen-bonded groups (-OH, -NH$_2$), and an
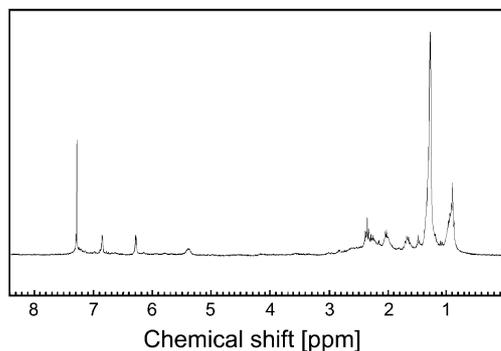
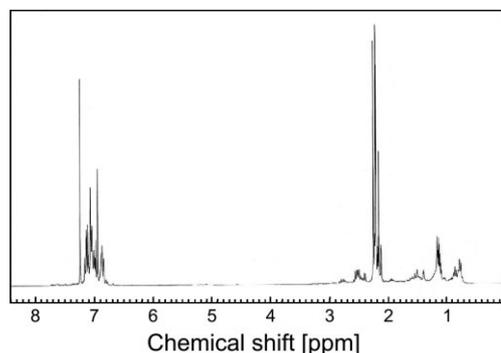

Figure 6. ^{1}H-NMR of bio-crude from meat and bone meal (T = 400 °C).

Figure 7. ^{1}H-NMR of bio-fuel from animal fat, T = 550 °C in the presence of Pentasil (WHSV = 2.0 h^{-1}, yield = 31.5 %, NCV = 40.1 MJ/kg).

absorption at 1.707 cm^{-1} due to the carbonyl groups (=C=O) confirming the presence of carboxylic acids and acyl derivatives. Thus, under bench experimental conditions, both the fatty acids and the functional derivatives of the carboxylic acids formed are not completely converted to hydrocarbons. In contrast, these peaks are missing in the IR-spectra of bio-fuels from animal fat using the zeolite Wessalith as an external catalyst at 400 °C (see Fig. 9). Thus, the catalytic conversion of fatty acids to hydrocarbons has been more effective by using the external zeolite catalysts.

Combustion experiments with bio-fuel from animal fat showed similar properties and emission values as the conventional heating oil under the same conditions [13].
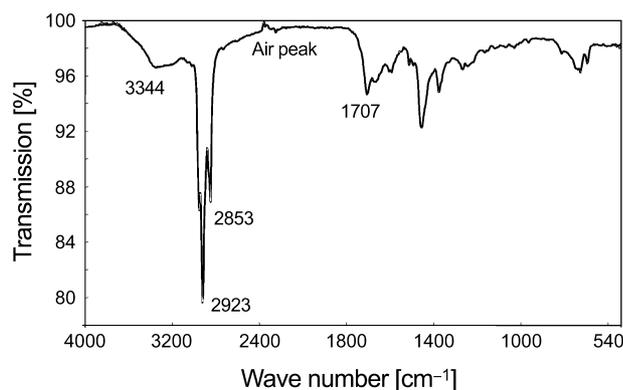

Figure 8. FTIR-spectrum of bio-crude produced by LTC from MBM at 400 °C.
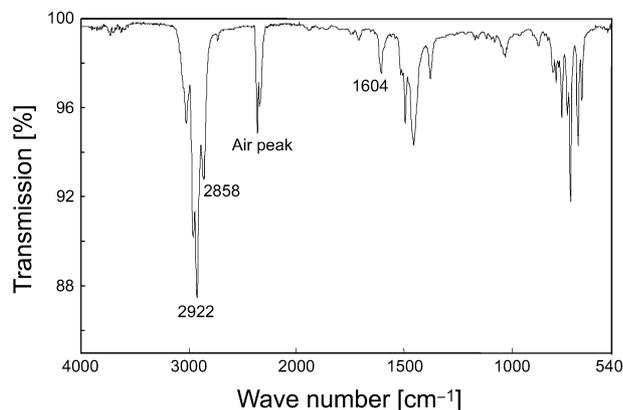

Figure 9. FTIR spectrum of bio-fuel from animal fat using Zeolite Wessalith as a catalyst at 400 °C. (Note differences in the 3.350 and 1.700 cm^{-1} regions in comparison to Fig. 8).

3.3   Solid Product

^{13}C-NMR of residual solids from the conversion of animal meal reveals 85 % of elemental carbon in the form of graphite (C: sp^2 hybridization) [12], which could be of interest to the carbon manufacturing industry.
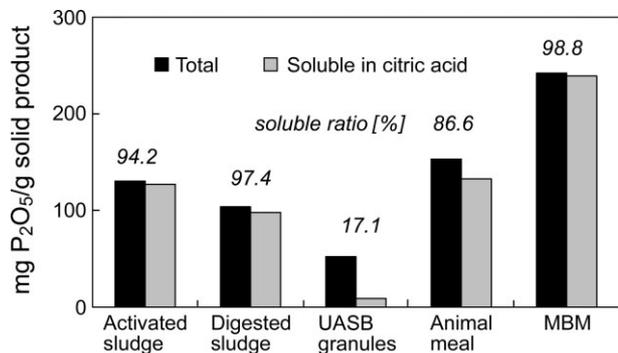
Figure 10. Recovery of phosphorus from different residual solids.

The total phosphorus content of solid products ranges between 50 to 242 mg P_2O_5/g. The latter value could be found in the solid product from MBM. This amount is comparable to mineral phosphorus resources.

In extracting the solids with 2 % citric acid, phosphorus may be recovered and available for plants. This is especially interesting for the solid product from MBM (see Fig. 10), wherein 98.8 % of phosphorus content is potentially available. In comparing pot experiments with LTC, the solid product of MBM was used as fertilizer and applied to the plant species Deutsches Weidelgras. The results demonstrated a 110 % plant growth with the LTC fertilized sample in proportion to the non-fertilized sample for a given P_2O_5 concentration of 1 g/kg. Nevertheless, plant growth of 85 % in comparison with a similar mineral fertilization was detectable. Plant growth was comparable to that obtained with other organic fertilizers [11].

3.4 Non-condensable Gas and Reaction Water

Qualitative analyses of the gas phase show CO_2, H_2 and C_1 to C_3 hydrocarbons as the main products, which will be used for the generation of process energy in future applications.

In the reaction water, formic, acetic and propionic acid as well as NH_4^+ and HCO_3^- are identified as the main constituents. The chemical oxygen demand of the reaction water from MBM (with a yield of 11.6) exhibits a COD = 257 g/L, the biological oxygen demand ends in a BOD = 80 g/L, and the concentration of ammonia is $[NH_4\text{-}N]$ = 7.2 g/L. The COD and BOD of the reaction water from animal meal (with a yield of 14.2 %) are in the same range, $[NH_4\text{-}N]$ = 88.0 g/L, whereas in the case of animal fat, the yield of reaction water is just 6.4 % with a COD of 19 g/L and BOD of 15 g/L, $[NH_4\text{-}N]$ = 1.6 g/L [12].

Regarding the high amounts of COD, BOD and $NH_4\text{-}N$ in the reaction water, especially from LTC of animal meal and MBM either a cycling of reaction water within the LTC plant or a downstream wastewater treatment seems to be necessary.

3.5 Energy Balance and Eco-efficiency

In the scope of an eco-efficiency analysis for the LTC process, both economic as well as environmental aspects are presently

under investigation. The energy balance of the LTC process shows a surplus of more than 14 GJ/Mg in the case of the conversion of 1 Mg of animal meal assuming a dry matter content of 95 %.

Prices for bio-fuel (chemically a hydrocarbon) from animal fat are in the range of 0.9 to 1.0 Euro per liter, depending on the quality of animal fat used for the conversion and efficiency of the plant operation. This range seems to be competitive to mineral oil or bio-diesel (methyl or ethyl ester of fatty acids) in many countries.

The hydrocarbon path avoids both production of methanol or ethanol for transesterification, surplus glycerol as well as precipitation of alkylesters of octadecanoic acid in bio-diesel from animal fat in winter. Stearic acid is a main component in many animal fats.

Decisive for sustainability of the LTC-technology is the fate of trace contaminants and recalcitrant compounds like pharmaceuticals, disinfectants, PCDD, PCDF, and PCB.

4 Conclusions

Prices for mineral oil on the world market are constantly increasing. This global trend calls for environmentally friendly alternatives such as biomass-to-liquid-fuel-technologies. In this respect, organic residues, besides agricultural products, are promising raw materials. A high amount of volatile solids and a low percentage of heteroatoms present in the substrate favorably affect the yield and caloric qualities of liquid hydrocarbons produced by LTC.

There is a market for high-grade fuel from renewable raw resources as long as the established quality and safety criteria are fulfilled on a self-sustaining economic basis.

The results from the catalytic conversion of animal fat in a prototype plant with a capacity of 5 kg/h will be reported at a later date.

Acknowledgements

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