Summary

Triglycerides are the main chemical components of plant and animal oils and are important feeds for the oleochemical industry. Global interest in triglycerides has increased dramatically in the last decade. This is mainly due to the production of biodiesel from triglycerides, which was estimated at 24.7 million ton in 2013. The biodiesel production in Europe has increased exponentially in the period 2000-2011 and is considered of high importance to meet the EU objective of a 10% biofuels share in the transportation sector by 2020. In the US, the biodiesel industry recorded nearly 6 million ton in 2013. Apart from biodiesel, triglycerides also have high potential for the production of (novel) biobased polymers, a market segment which is expected to grow to 12 million ton by 2020.

The main objective of the research presented in this thesis is to identify interesting biobased products from the seeds of the rubber tree (*Hevea brasiliensis*). The seeds are of particular interest as they are currently not valorised and regarded as waste. Potentially interesting products are rubber seed oil and the protein rich press cake after isolation of the oil. From a biorefinery perspective, the identification of high added value products from the rubber seeds is highly relevant as it increases the profit for the rubber value chain. The research activities are complemented with activities using jatropha and sunflower oil. The former has high potential to become a major global plant oil in the coming decades, whereas sunflower oil was mainly used as a model oil that is easily accessible in high purity.

In Chapter 2, experimental and modelling studies on the isolation of rubber oil from rubber seeds using a laboratory scale hydraulic press in both the absence and presence of a solvent are reported. The effect of seed moisture content, temperature, pressure and solvent to seed ratio on the oil yield was investigated. The experimental data set was modelled using two approaches, viz i) a fundamental model known as the Shirato model and ii) a regression model using a statistical approach. An optimum oil recovery of 76 wt% was obtained using ethanol as the solvent (1.6 wt% rubber seeds, 14 vol/wt% ethanol, 20 MPa, 75 °C, 10 min pressing time). Relevant properties of the rubber seed oil obtained at optimum conditions were determined. The rubber seed oil has a relatively low acid value (2.3 mg KOH/g) and is a suitable feed for the base catalysed biodiesel synthesis.

In Chapter 3, experimental studies on the effects of rubber seed storage conditions (humidity and time) on relevant properties of the pressed rubber seed oil are reported. The acid value of the isolated rubber seed oil after 2 month seed storage increased slightly to values up 4.19 mg KOH/g. The effect of storage time (27 °C, closed container) on the acidity of the rubber seed oil and rubber seed ethyl esters was also evaluated.
Freshly isolated rubber seed oil and rubber seed ethyl esters derived thereof were shown to have a relatively low acid value of 0.52 and 0.32 mg KOH/g respectively. The acid value of rubber seed oil only slightly increased during storage (0.52 to 0.60 mg KOH/g), whereas the acid value of the rubber seed ethyl esters (0.32 to 0.33 mg KOH/g) was about constant. These results indicate that it is better to store the rubber seed oil or the esters thereof than the seeds. In addition, moisture uptake/release versus time profiles for rubber seeds were determined at 27 °C and a relative humidity of 67% for a period of two months. The moisture versus time curves were modelled using an analytical solution of the instationary diffusion equation and allowed the determination of the diffusion coefficient of water in the rubber seeds at 27 °C.

In Chapter 4, the synthesis and refining of biodiesel from sunflower oil and methanol in a cascade of continuous centrifugal contactor separators (CCCS) is described. The effect of relevant process variables like oil and methanol flow rate, rotational speed and catalyst concentration was investigated and modelled using non-linear regression. At optimised conditions (oil flow rate of 31 mL/min, rotational speed of 34 Hz, catalyst concentration of 1.2 wt% and a methanol flow rate of 10 mL/min), the biodiesel yield was 94 mol% at a productivity of 2470 kg FAME/m$^3_{\text{reactor}.h}$. Proof of principle for the synthesis and subsequent refining of biodiesel in a cascade of two CCCS devices is also reported.

In Chapter 5, experimental and modelling studies on continuous biodiesel synthesis and refining in a dedicated bench scale unit are reported. The setup consists of three major sections: i) a CCCS reactor/seperator, ii) a crude biodiesel water wash and iii) a biodiesel drying unit using air. The concept was demonstrated for the methanolysis of sunflower oil using sodium methoxide as the catalyst. The effect of process conditions like flow rates, temperature, acidic water and water to biodiesel ratio was investigated. The highest attainable sunflower oil throughput for a conversion of at least 95 mol% was 32 mL/min (7.5:1 molar excess to oil and 1.2 wt% of catalyst regarding to the oil 70 °C, 35 Hz), leading to a FAME productivity of 2460 kg FAME/m$^3_{\text{reactor}.h}$. The bench scale unit was modelled using Aspen and agreement between experimental data and the Aspen model was very satisfactory.

The proof of principle for the ethanolation of Jatropha curcas L. oil in a batch reactor and a CCCS is provided in Chapter 6. The effect of process variables like catalyst concentration, rotational speed, oil flow rate and ethanol to oil molar ratio was investigated for the synthesis of ethyl-esters (FAEE) from jatropha oil in a CCCS. Maximum FAEE yield was 98 mol% for both the batch (70 °C, 600 rpm, 0.8 wt% of sodium ethoxide) and CCCS reactor configuration (60 °C, 2100 rpm, 1 wt% of sodium ethoxide, oil feed 28 mL/min). The volumetric production rate of FAEE in the CCCS at optimum conditions was 112 kg$\text{FAEE}/m^3_{\text{liquid}.min}$.  

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In Chapter 7, the synthesis of cross-linked biobased polymers from epoxidized rubber seed oil and triethylenetetramine is described. The effect of relevant reaction conditions such as time, temperature, pressure and the molar ratio of the epoxide to the primary amine groups was investigated and modelled using non-linear regression. Good agreement between experiments and model was obtained. At optimised conditions, the cross-linked biobased polymer has a $T_g$ of 11.1 °C with a tensile strength and strain at break of 1.72 MPa and 182%, respectively. These values are higher than obtained for polymers derived from epoxidised soybean, jatropha, palm and coconut oil and for a commercial sample of an epoxidised soybean oil.

Preliminary techno-economic evaluations on a rubber seed expeller unit and a biodiesel unit in central Kalimantan (Palangkaraya) are presented in Chapter 8. The production costs for rubber seed oil in a small-scale rubber seed expeller unit were estimated to be €0.42/L (55 ton/y). As such, the oil has economic potential to replace diesel in stationary diesel engines, e.g. for electricity generation. Sensitivity analysis reveals that the capital investment costs have a relatively minor impact on the production costs of the RSO. Thus, optimisation of the design and reduction of the equipment costs should not be considered as a major research and development topic. The major variable is the amount of RSO produced in the unit. In addition, the total production cost for biodiesel production at small scale (55 ton/y) from RSO using CCCS technology was also evaluated and found to be €1.00/L. This value is comparable to the price of diesel in remote areas in the ex-mega rice project area close to Palangkaraya, Indonesia (up to €1.25/L).