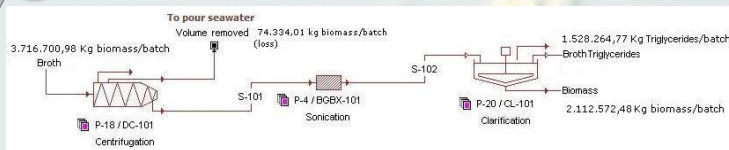


1

## Stage 1: Triglyceride separation



Photobioreaction broth contains algal biomass diluted with seawater (reaction medium). A 90% of this water is removed in a centrifugation step (volume removed stream). Then a sonication treatment step is carried out in order to lyse *Dunaliella* cells to release their oil content (triglycerides). Finally, sonicated broth is clarified so that triglycerides will remain in the supernatant (Broth Triglycerides stream) whereas non-lipidic particles will settle at the bottom of the clarifier (Biomass stream).

### EQUIPMENT

Decanter centrifuges Industrial sonicators



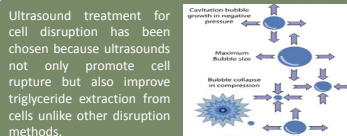
Clarifiers



STAGE'S YIELD

$$\eta = 97.90\%$$

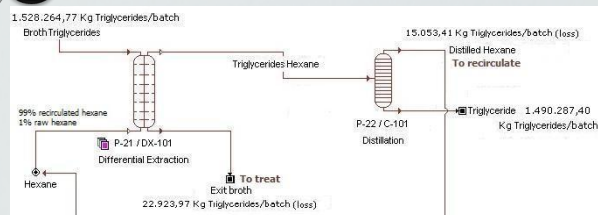
### Ultrasound for cell lysis



Intense sonication produces cavitation inside cells and the resulting shear forces break the cell structure and improve mass transfer. This allows triglycerides to be extracted easily (1).

2

## Stage 2: Triglyceride purification



STAGE'S YIELD

$$\eta = 97.51\%$$

Broth's triglycerides have to be purified and separated from the seawater. So, a liquid-liquid extraction is carried out where triglycerides go from heavy (seawater) to light phase (hexane) because their better solubility in hexane. The light phase stream is then distilled to separate the triglycerides from the hexane. Due to the difference of the boiling points of these compounds (2), triglycerides are obtained highly concentrated. The use of hexane as a solvent allows obtain recovery yields of 98% (3). Distilled hexane is recirculated to the extraction column input.

### Hexane as a solvent

The reason why hexane is used as a solvent is its popularity, its low cost and its good miscibility in lipid molecules. Other reasons for their use are that it doesn't cause greenhouse gas or carcinogenic problems. The fact that hexane is only a good solvent for low polarity lipids must be taken into a count (3).

### Reuse of hexane

Hexane separated by distillation is condensed and then recirculated so as to be reused as extraction column light phase. For each recirculation cycle, a 1% of recirculated mass flow is renewed for raw hexane (make-up).

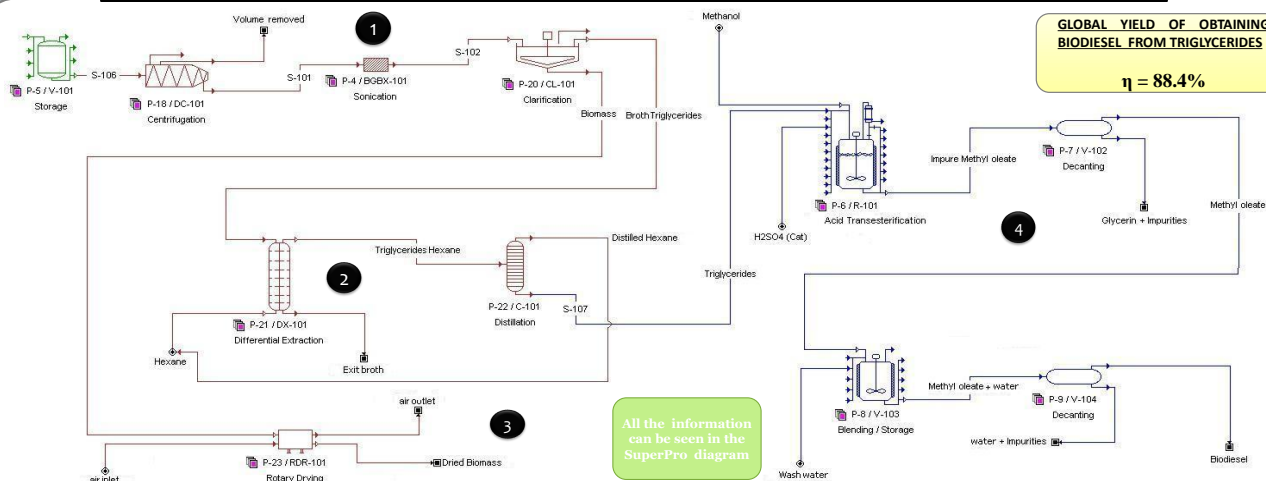
### EQUIPMENT

Differential extractors

Distillation column



## FLUX DIAGRAM OF DOWNSTREAM AND TRANSESTERIFICATION



GLOBAL YIELD OF OBTAINING BIODIESEL FROM TRIGLYCERIDES

$$\eta = 88.4\%$$

### An energetic by-product

Each year 1875.61 tons of glycerin are produced as a transesterification by-product.

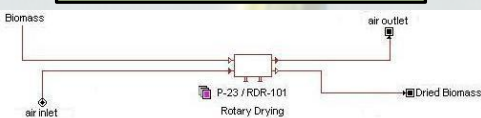
Considering that the purity of the glycerin is 70%, combustion of this glycerin could produce 6929.35 kWh per year.

This amount of energy is equivalent to the amount of energy needed to illuminate UAB during 1.6 hours.



3

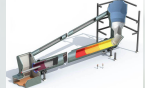
## Stage 3: Biomass drying



*Dunaliella* disrupted biomass which has settled during clarification is a process's by-product that can be used and sold. Therefore, seawater must be removed from biomass in a drying step using a heated air stream. In this way we obtain dried biomass of *Dunaliella* biomass (which contains approximately 2% of  $\beta$ -carotene).

### EQUIPMENT

Cement kiln

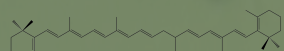


### ECONOMIC DRYING

Algal biomass has to be dried if it is to be sold. To save economical costs, it is decided using a cement kiln not in use to dry disrupted biomass by using the combustion exhaust gases from the operating kiln. This saves the cost of a dryer and air heating

### *D. tertiolecta* biomass as a source of $\beta$ -carotene

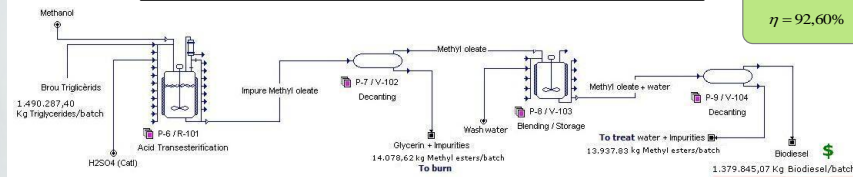
*D. tertiolecta*  $\beta$ -carotene is distributed today in many different markets under 3 different categories:  $\beta$ -carotene extracts, *Dunaliella* powder for human use and dried *Dunaliella* for animal feed or food colorant.



This biomass is sold. It is shipped under vacuum in bags for feed coloration or for feed in cattle, poultry, fishes, shrimps and more (4).

4

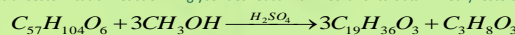
## Stage 4: Transesterification process



STAGE'S YIELD

$$\eta = 92.60\%$$

In order to obtain fatty acid methyl esters (which mixture will end up being biodiesel), triglycerides have to react with methanol in an acid transesterification reaction. Triglycerides react with methanol to obtain methyl esters and glycerin governed by this stoichiometry:



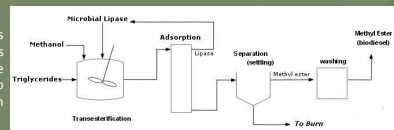
Sulfuric acid acts as a catalyst and allows a 99% of reaction conversion at concentration of 2,3% (v/v) and in a reaction time of 24 hours.

Glycerin (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>) and other impurities are separated from formed methyl esters in a decantation step where due to density differences, the methyl esters remain in the light phase. Then, a wash with water of methyl esters is carried out using mixer-settler equipment. Finally, pure methyl esters which have been separated in this last step are obtained, becoming biodiesel ready to use (5).

### Alternative: Enzymatic transesterification

There is a research branch focused in the use of enzymes for catalyzing transesterification reactions. The advantages of using enzymes instead of chemical catalyzed method are that enzymes allow mild reaction conditions, don't need to be in an aqueous media necessarily (excellent to transform triglycerides) and they are selective (6).

The most promising enzymes are microbial lipases.



Hypothetical block diagram of an enzymatic transesterification process

### EQUIPMENT

Stirred Reactors

Decanter tanks

Blending tanks

## Selected References

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## Conclusions

- Only a 24.2% of the expected annual production of biodiesel is achieved. This process has a commitment with environmental safety
- A high yield of biodiesel obtained from vegetable oils has been reached
- Although enzyme-catalyzed transesterification processes are being developed, is more feasible carry out an acid transesterification
- Using by-products to reduce plant costs has allowed us estimate a biodiesel selling price lower than expected. And so, keep dreaming that the consecration of the use of microalgae as a renewably source of energy will be soon a reality.