Biodiesel

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Significance

- Biodiesel is an important biofuel alternative to diesel.
- Biodiesel can be blended to petroleum-derived diesel.
- Biodiesel can offer energy and economic security of developing nations, if produced locally from indigenous biomass (bio-based waste resource).
- Its application is as fuel: automotive, marine, agriculture and power generation.
- Anhydrous biodiesel production is feasible from used cooking oil. This is a sustainable way to run diesel vehicle.
- First generation feedstocks such as vegetable oils: canola, palm, soybean, corn, etc. should be avoided for deforestation reasons. Waste oils and fats are alternative feedstocks. Algae are another feasible feedstock.

Sadhukhan J, Ng KS and Martinez-Hernandez E. 2014. Biorefineries and Chemical Processes: Design, Integration and Sustainability Analysis. Wiley.
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Sustainability

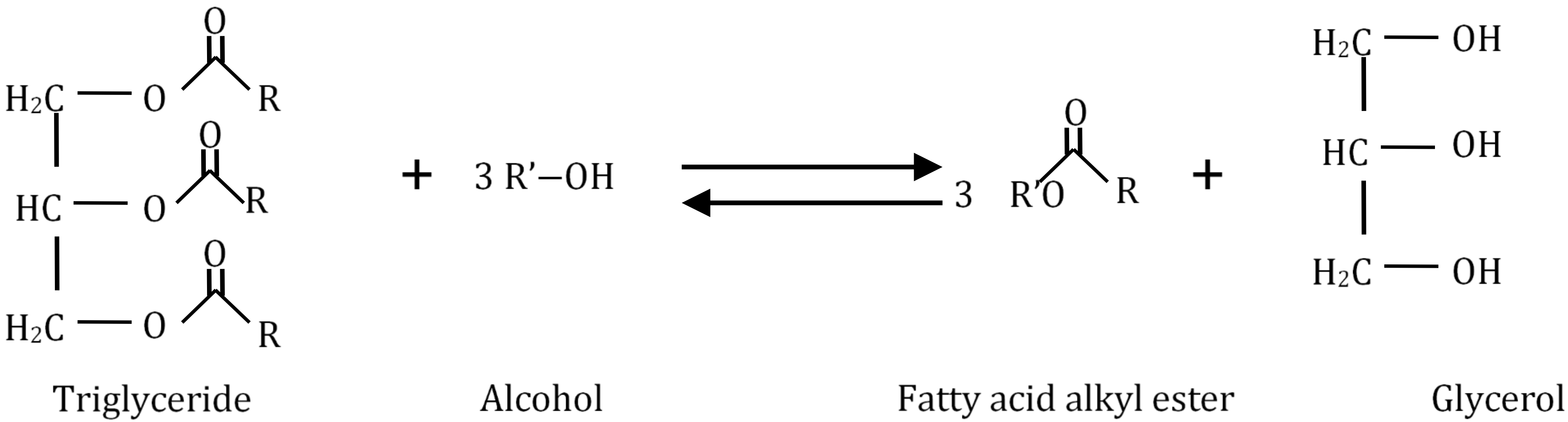
- Technical challenges: we have to ensure coproduction of high quality glycerol or glycerol derived chemical, with biodiesel as the main product where possible to maximise resource efficiency. An industrial process must not stop at the reactor stage. The process must include fractionator for methanol recovery and recycling to the reactor, decanter to recover glycerol and fractionator to purify biodiesel from residual stream. In addition, heat recovery network should be synthesized considering pinch analysis. Demands for heating, cooling and electricity for driving fluids around the process must be met by on-site combined heat and power generation system using the various organic containing streams in the process. Research has primarily focused on novel catalyst or catalytic reactor for converting triglycerides into fatty acid methyl esters (FAME) known as biodiesel. Our research has uniquely considered whole integrated process designs.

- Environmental challenges: Coproduction of glycerol or glycerol derived chemical is essential for sharing costs and environmental impacts. Non-food or waste feedstocks are needed to alleviate deforestation or biodiversity loss impacts

- Economic challenges: Coproduction shares cost of production and generates value on processing.

- Social challenges: Importing bioethanol to meet transport fuel demand means social cost especially from countries lower in the GDP per capita scale. There is dilemma however if foreign appreciation into less developing countries is avoided.

Transesterification reaction



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Common constituents of feedstock

Notation	Fatty acid	Formula	Triglyceride	Formula
[C12:0]	Lauric acid	$C_{12}H_{24}O_2$	Trilaurin	$C_{39}H_{74}O_6$
[C14:0]	Myristic acid	$C_{14}H_{28}O_2$	Trimyristin	$C_{45}H_{86}O_6$
[C16:0]	Palmitic acid	$C_{16}H_{32}O_2$	Tripalmitin	$C_{51}H_{98}O_6$
[C16:1]	Palmitoleic acid	$C_{16}H_{30}O_2$	Tripalmitolein	$C_{51}H_{92}O_6$
[C18:0]	Stearic acid	$C_{18}H_{36}O_2$	Tristearin	$C_{57}H_{110}O_6$
[C18:1]	Oleic acid	$C_{18}H_{34}O_2$	Triolein	$C_{57}H_{104}O_6$
[C18:2]	Linoleic acid	$C_{18}H_{32}O_2$	Trilinolein	$C_{57}H_{98}O_6$
[C18:3]	Linolenic acid	$C_{18}H_{30}O_2$	Trilinolenin	$C_{57}H_{92}O_6$

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Catalyst for biodiesel synthesis

The transesterification reaction requires a catalyst to achieve high reaction rate and high conversion. Alkalis such as NaOH, KOH and methoxides such as $NaOCH_3$ are the most commonly used homogeneous catalysts. Typical catalyst concentration is about 1% by weight of oil. The reaction is carried out at 60°C under atmospheric pressure. Yield of methyl esters may exceed 98% on a weight basis. Despite being widely established, the **homogeneously catalysed reaction** makes downstream processing more complex: i) requires additional reaction to neutralise the alkali, which generates a salt waste; ii) the glycerol produced is of low quality and requires further purification; iii) a water washing step is required to remove glycerol and catalyst for biodiesel purification.

Heterogeneously catalysed transesterification facilitates downstream processing thus enhancing operation efficiency and reducing production costs and environmental impact. Solid heterogeneous catalysts may require much higher alcohol-to-oil molar ratios and higher operating temperatures than homogeneous catalyst, but they are easily separated from the product or can be fixed in a catalyst bed within the rector. This avoids the need for the neutralisation and water washing steps. In addition, the glycerol produced has a higher purity. Common heterogeneous catalysts include metal oxides such as CaO, ZnO, MgO, metal carbonates, zeolite type catalysts, polymeric resins and enzymes. Zirconium and titanium based catalyst have also been tested. Heterogeneous catalysts could also achieve complete conversion of free fatty acids and eliminate soap formation (a common issue in homogeneous alkali catalysts). This capability provides higher feedstock flexibility to the biodiesel process.

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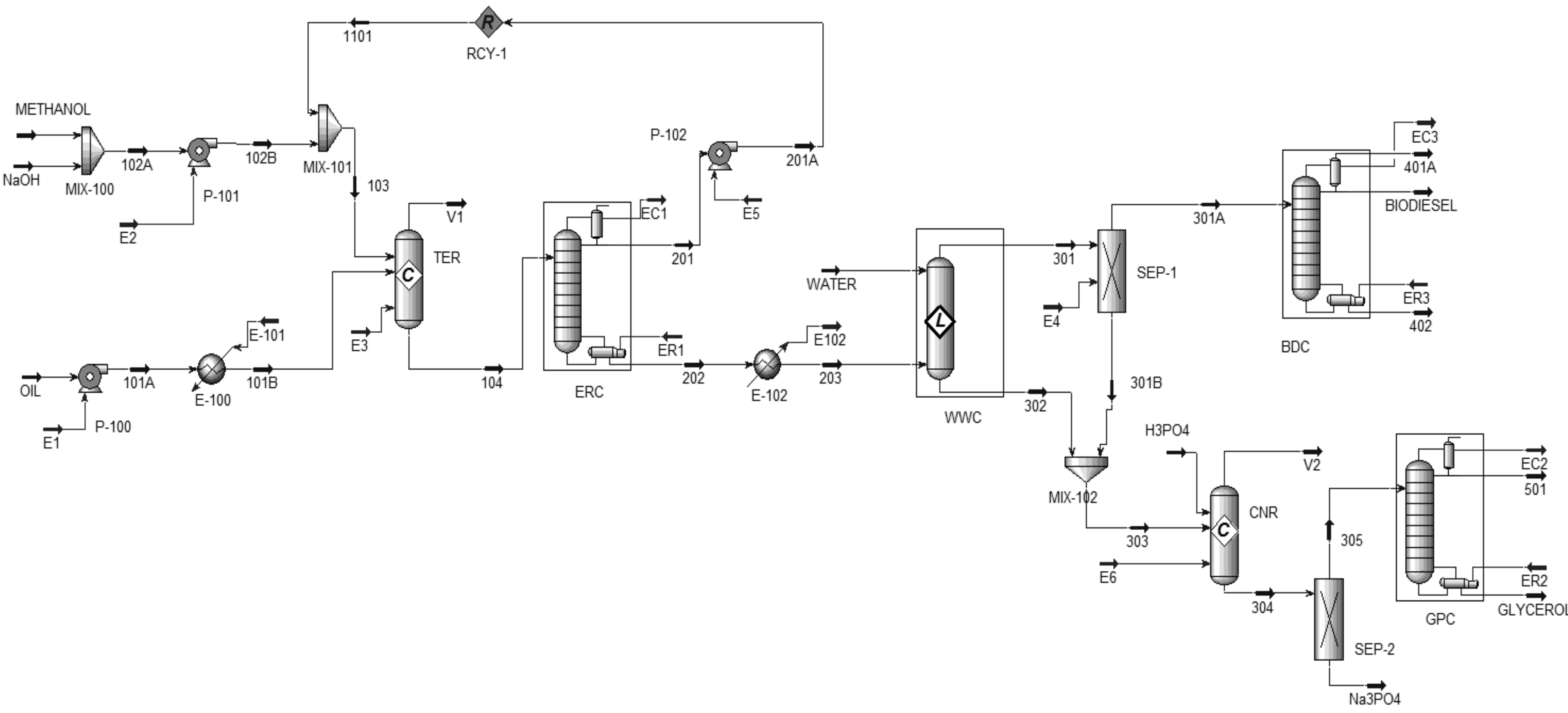
Integrated process



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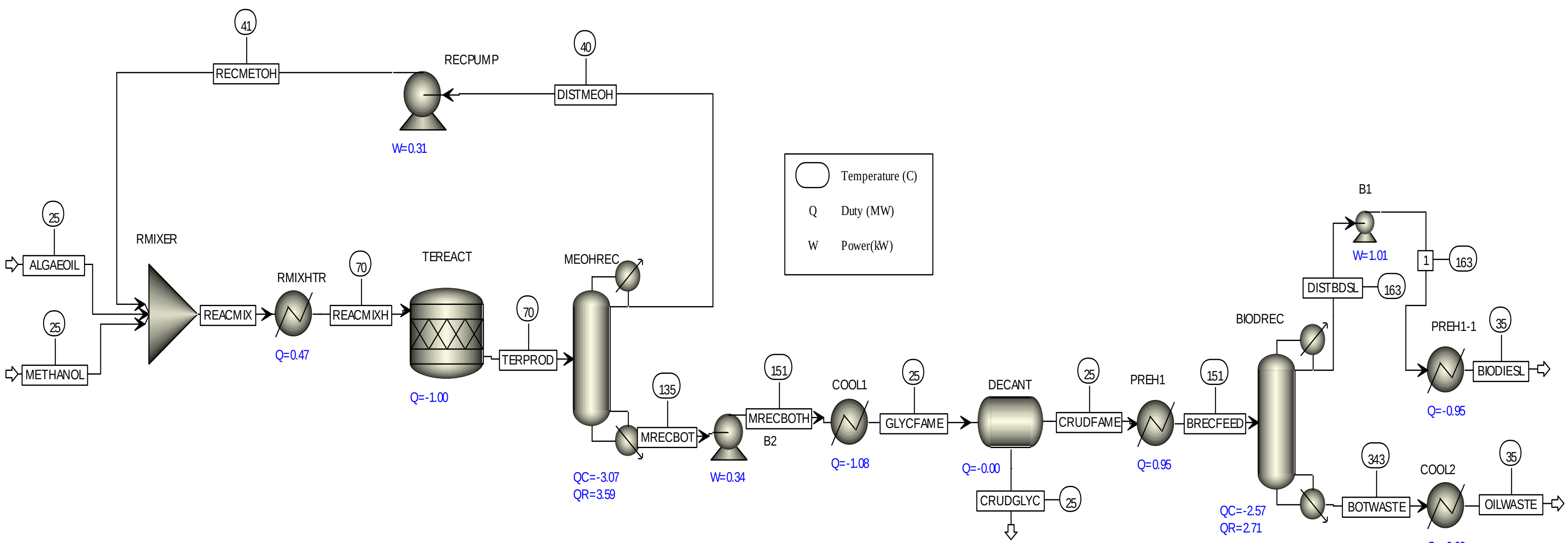

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Stream results from process simulation

Stream name	ALGAEOIL	METHANOL	RECMETOH	TERPROD	MRECBOT	GLYCFAME	CRUDFAME	OILWASTE	BIODIESL	CRUDGLYC
From	Feed	Feed	RECPUMP	TEREACT	MEOHREC	COOL1	DECANT	COOL2	PREH1-1	DECANT
To	RMIXER	RMIXER	RMIXER	MEOHREC	B2	DECANT	PREH1	Waste	Product	Product
Component	Mass fractions									
3OLEIN	0.6647	0.0000	0.1712	0.0357	0.0000	0.0000	0.0000	0.0012	0.0000	0.0000
3PALMITI	0.1175	0.0000	0.0000	0.0059	0.0074	0.0074	0.0082	0.2642	0.0000	0.0000
3LINLEIN	0.1542	0.0000	0.0000	0.0077	0.0097	0.0097	0.0107	0.3467	0.0000	0.0000
3STEARIN	0.0314	0.0000	0.0000	0.0016	0.0020	0.0020	0.0022	0.0706	0.0000	0.0000
OLEIC-01	0.0322	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
M-OLEATE	0.0000	0.0000	0.0000	0.5003	0.6319	0.6319	0.6966	0.1458	0.7142	0.0000
MPALMTTE	0.0000	0.0000	0.0000	0.0783	0.0989	0.0989	0.1091	0.0750	0.1101	0.0000
MLINLEAT	0.0000	0.0000	0.0000	0.1027	0.1298	0.1298	0.1431	0.0107	0.1473	0.0000
MSTEARAT	0.0000	0.0000	0.0000	0.0209	0.0264	0.0264	0.0291	0.0847	0.0274	0.0000
METHANOL	0.0000	1.0000	0.8286	0.1743	0.0022	0.0022	0.0006	0.0000	0.0006	0.0178
GLYCEROL	0.0000	0.0000	0.0000	0.0711	0.0898	0.0898	0.0000	0.0010	0.0000	0.9655
WATER	0.0000	0.0000	0.0002	0.0015	0.0018	0.0018	0.0003	0.0000	0.0003	0.0167
Total Flow (kmol h^{-1})	1.54	4.34	9.61	15.49	5.88	5.88	4.32	0.07	4.25	1.56
Total Flow (kg h^{-1})	1262.6	139.0	368.7	1770.4	1401.6	1401.6	1271.4	39.3	1232.1	130.2
Temperature (°C)	25	25	41	70	135	25	25	35	35	25
Pressure (kPa)	202.7	202.7	202.7	101.3	50.0	101.3	101.3	101.3	101.3	101.3
Density (g cm^{-3})	1.0967	0.7929	0.7780	0.0683	0.7691	0.8945	0.8697	0.9290	0.8642	1.2661

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Biodiesel properties

Property	Units	EN 14214:2008	ASTM D6751	Simulation
Density @ 15°C	g cm^{-3}	0.86-0.9		0.8782
Viscosity @ 40°C	mm^2 s^{-1}	3.5-5.0	1.9-6.0	4.47
Cetane number	-	min 51	min 47	58.5
Flash point	°C	>101	min 130	FLPT-API method: 135.9 FLPT-R4 method: 162.4
FAME content	% mass	min 96.5		99.9
Water content	% mass	max 0.5	max 0.5	0.03
Triglycerides content	% mass	max 0.2		0.00
Glycerine content	% mass	max 0.25	max 0.24	0.00
Methanol content	% mass	max 0.2		0.06

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Example feedstock compositions

Algae biomass fraction	Mass content (%)
Oil	35
Protein	25
Starch	20
Nitrogen	5
Phosphorous	1
Others	14

Component	Mass fraction
Triolein	0.6647
Trilinolein	0.1542
Tripalmitin	0.1175
FFA (as oleic acid)	0.0322
Tristearin	0.0314

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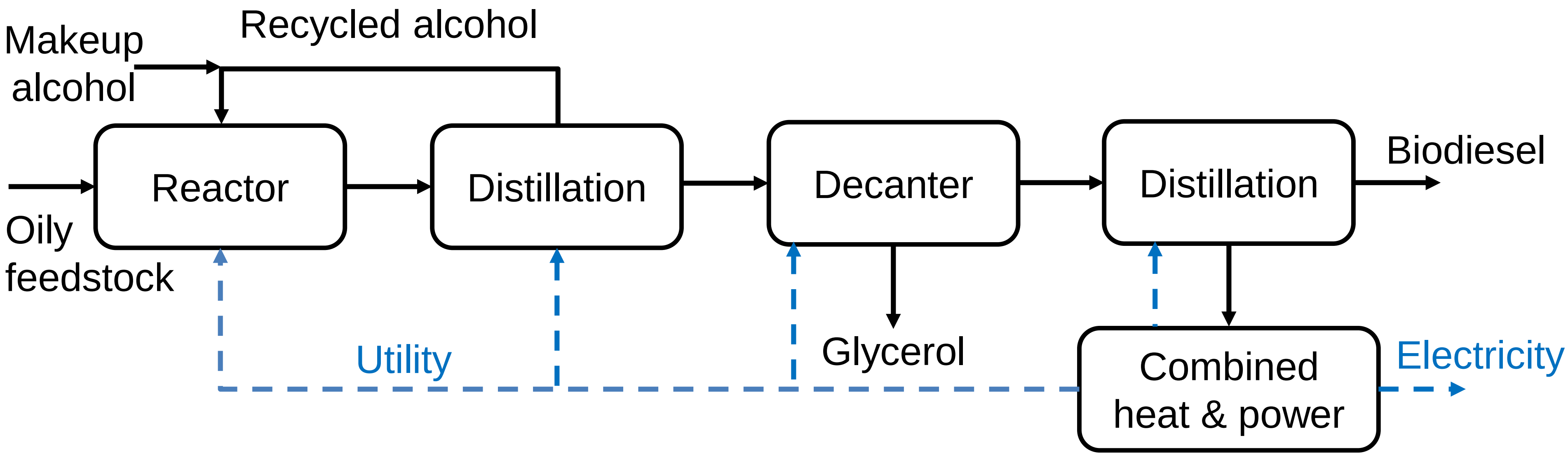
Key unit processes



Biodiesel: 0.9 × triglyceride in feedstock + fatty acid in feedstock (mass basis)
Glycerol: 0.1 × triglyceride in feedstock (mass basis)
Fuel to CHP: 0.03 × (triglyceride in feedstock + fatty acid in feedstock) (mass basis)
Calorific value of fuel to CHP: 16 MJ/kg fuel to CHP
Boiler efficiency: 0.8
Heat (low grade) demand: 0.33 MJ/kg biodiesel
Heat to electricity conversion efficiency: 0.28
Electricity demand: 0.08 kJ/kg biodiesel
Makeup methanol: 0.11 kg/kg biodiesel

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Economic Analysis

- **Economic Margin** = Value of products – Operating cost – Capital cost
- **Netback** (when feedstock cost is unknown) = Value of products – Operating cost w/o Cost of feedstock – Capital cost
- **Cost of production** (when product price is unknown) = Operating cost + Capital cost

Cost components

- Capital cost (Annual)
  - Delivered cost of equipment
  - Direct
  - Indirect
  - Working capital
  - Total capital investment
  - Annual capital charge

- Operating cost
  - Fixed
  - Variable

Correlation between delivered cost of equipment and size

$$\frac{\mathrm{COST}_{\mathrm{size2}}}{\mathrm{COST}_{\mathrm{size1}}} = \left(\frac{\mathrm{SIZE}_2}{\mathrm{SIZE}_1}\right)^R$$

where

SIZE_1 is the capacity of the base system, t/h or t/y,

SIZE_2 is the capacity of the system after scaling up/down, t/h or t/y,

$\mathrm{COST}_{\mathrm{size1}}$ is the cost of the base system, €,

$\mathrm{COST}_{\mathrm{size2}}$ is the cost of the system after scaling up/down, €,

R is the scaling factor.

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Apply Capital Cost Index

$$C_{pr} = C_o \left(\frac{I_{pr}}{I_o} \right)$$

where

C_{pr} is the present cost.
C_o is the original cost.
I_{pr} is the present index value.
I_o is the original index value.

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Capital cost

Plant	Solid Processing	Solid–Fluid Processing	Fluid Processing
Direct Cost			
Delivered cost of equipment	1.00	1.00	1.00
Installation	0.45	0.39	0.47
Instrumentation and control	0.18	0.26	0.36
Piping	0.16	0.31	0.68
Electrical systems	0.10	0.10	0.11
Buildings (including services)	0.25	0.29	0.18
Yard improvements	0.15	0.12	0.10
Service facilities	0.40	0.55	0.70
Total direct cost, C_D	**2.69**	**3.02**	**3.60**
Indirect Cost			
Engineering and supervision	0.33	0.32	0.33
Construction expenses	0.39	0.34	0.41
Legal expenses	0.04	0.04	0.04
Contractor's fee	0.17	0.19	0.22
Contingency	0.35	0.37	0.44
Total indirect cost, C_{ID}	**1.28**	**1.26**	**1.44**
Working capital	0.7	0.75	0.89
Total capital investment, C_{TCI}	**4.67**	**5.03**	**5.93**

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Operating cost

Fixed operating cost dependent on indirect capital cost		
Maintenance	5-10%	of indirect capital cost (annualised)
Capital charges	10%	of indirect capital cost (annualised)
Insurance	1%	of indirect capital cost (annualised)
Local taxes	2%	of indirect capital cost (annualised)
Royalties	1%	of indirect capital cost (annualised)
Fixed operating cost dependent on personnel cost		
Personnel	52033	$ per t/h product bioethanol
Laboratory costs	20%	of personnel cost
Supervision	20%	of personnel cost
Plant overheads	50%	of personnel cost
Total fixed operating cost = Fixed operating cost dependent on indirect capital cost + Fixed operating cost dependent on personnel cost		
Total operating cost = 1.3 × (Total fixed operating cost + Variable operating cost)		

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Indirect capital cost

To calculate the fixed operating cost, indirect capital cost must be known, shown as follows:

Indirect Capital Cost		
Item	Factor	
Engineering and supervision	0.32	
Construction expenses	0.34	
Legal expenses	0.04	
Contractor's fee	0.19	
Contingency	0.37	
Total	1.26	Times annualised Delivered cost of equipment

Environmental impact savings

- In the current policy landscape, the final use of biomass for energy and transportation fuel is considered to be carbon neutral. This is because direct biogenic emissions from biomass end use are captured during growth completing the carbon cycle.
- If energy needed by biomass conversion process is supplied renewably e.g. by on-site generation, then emissions caused by burning fossil derived transportation fuel can be eliminated by using biofuel.
- Savings in various life cycle impact categories can be estimated from the difference in life cycle impacts between petrol and bioethanol for a given energy output.
- Impact saving factors have been deduced from the EU RED 2018.

Example of life cycle impact categories

Life cycle impact category	Unit (per GWh energy output)
Global warming potential	tonne CO_2 equivalent
Fossil resource depletion potential	GJ

Study References

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