Sustainable and integrated production of liquid biofuels, green chemicals and bioenergy from glycerol in biorefineries

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GLYFINERY partners

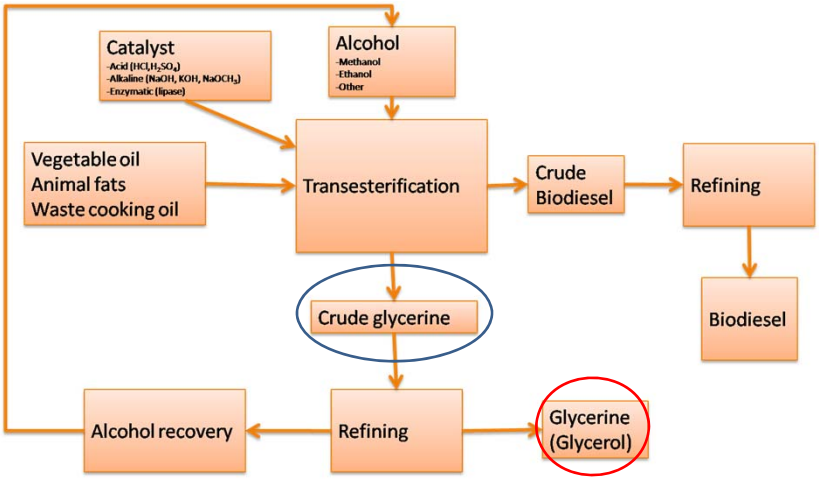
- Technical University of Denmark
- BioGasol ApS, Denmark
- A&A Biotechnology, Poland
- MEROCO, Slovakia
- The Institute for Energy and Environmental Research, Germany
- ProChimia Surfaces, Poland

Project period: March 2008 – February 2012

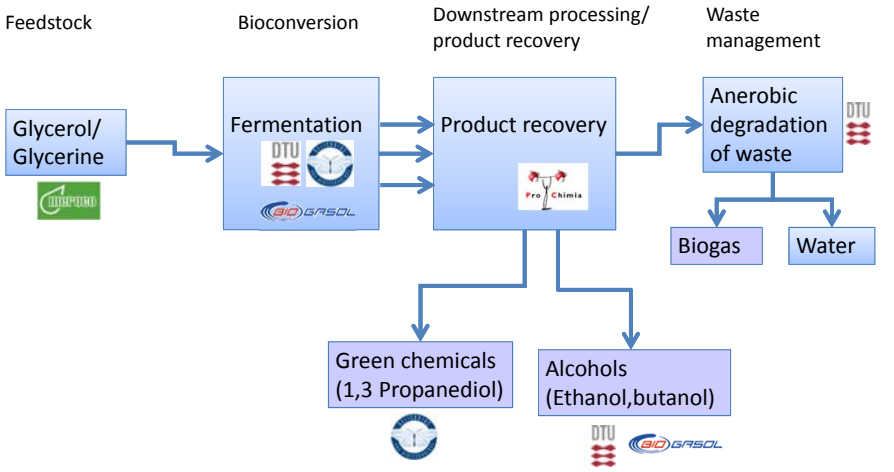
GLYFINERY project

- Targeted to development of novel technologies based on biological conversion of glycerol
- Aimed at producing new and known advanced liquid biofuels, bioenergy and biochemicals
- Development of new and efficient recovery processes
- Integrated biorefinery concept
- Guided by life cycle assessment (technical, environmental and economic)

Biodiesel production process



Integrated GLYFINERY concept



Life cycle analysis and assessment (technical, environmental, economic)

Target products

- Green chemicals

1,3 – propanediol, produced by *Clostridia* (A&A Biotechnology, Poland)

- Alcohols

Ethanol produced by yeast (DTU) B

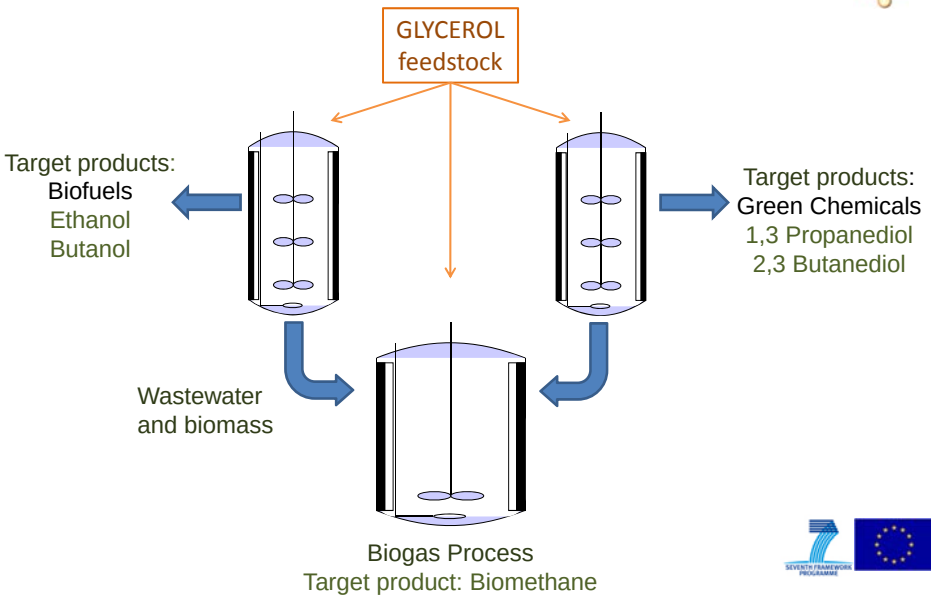
Butanol produced by *Clostridia* (BioGasol)

- Biogas

Biomethane (DTU)

Product recovery solutions (ProChimia Surfaces, Poland)

Target products



Production of liquid biofuels- DTU

- Screening of potential cell factories for conversion of glycerol
- Quantitative microbial physiology
- Fermentation optimisation

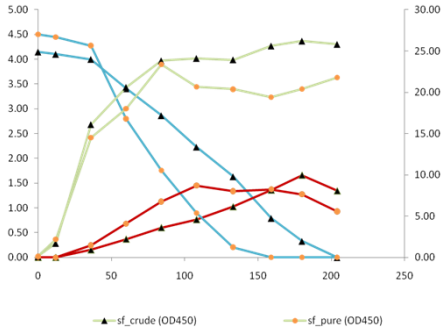
Three bioprocesses selected based on different yeasts: biodiesel, biochemicals and bioethanol

Bioethanol process

Pacchysolen tannophilus (a non-conventional yeast)

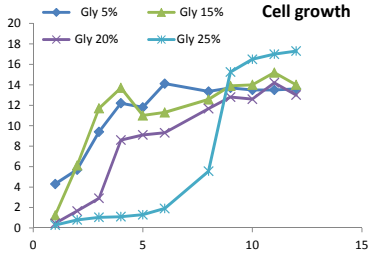
- Known producer of ethanol from D-xylose
- Previously shown to ferment glycerol (Maleszka, 1982)

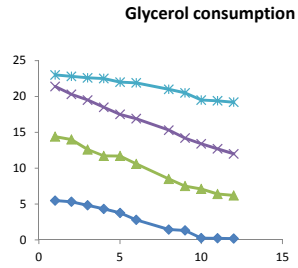
Bioconversion by *P. tannophilus*: Supply of glycerol

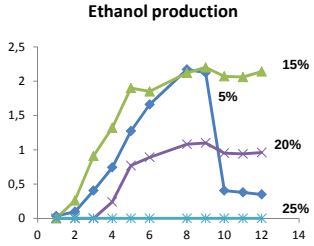


- Biodiesel industry typically uses variety of oil blends
- Meroco rape seed oil biodiesel
- Blends with used cooking oil
- *P . tannophilus* not affected by variations in glycerol batches from Meroco
- Robust process

P. tannophilus growth on glycerol







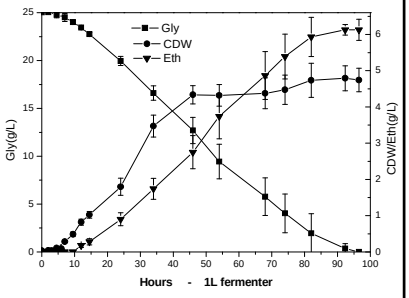
- *P. tannophilus* is capable of growing on 25% glycerol in small scale but no ethanol produced at this concentration.

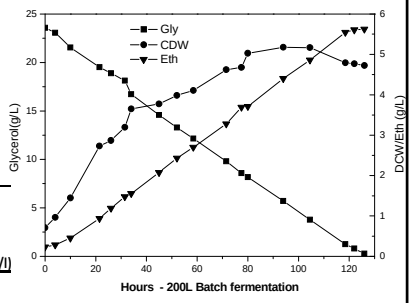
Liu, Jensen and Workman (2011) Bioresource Technology.
DOI: 10.1016/j.biortech.2011.10.065

P. tannophilus ethanol process lab scale and large scale

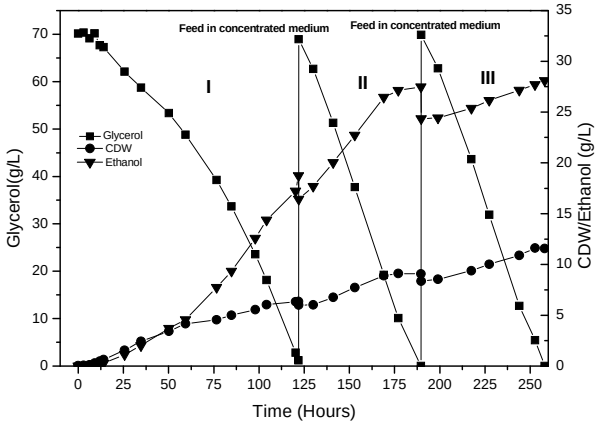
Sartorius 200 litre STR

Volume	Stirring speed (rpm)	Airflow (slpm)	Aeration (vvm)	pH	Biomass yield 2nd phase (g/g)	Ethanol yield (g/g)	Glycerol used (g/l)	Ethanol produced (g/l)
200L	150	20	0,1	5	0,1608	**0,2414**	**23,576**	**5,623**
0,6L	450	0,05	0,0833	5	0,064	**0,271**	**25,028**	**6,325**





Staged Batch Process



28.1 g/L glycerol achieved

Highest ethanol production obtained for a yeast species growing on glycerol

Liu, Jensen and Workman (2011) Bioresource Technology.
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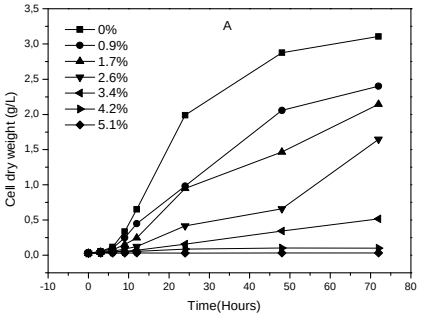
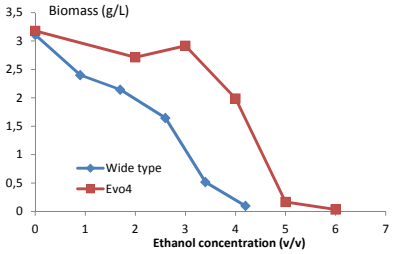
P. tannophilus - Ethanol tolerance



Further steps to increase ethanol tolerance by adaptive evolution

- Strain evolved which can tolerate 5.5% ethanol
- To be tested in fed-batch process



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Production of butanol - BioGasol

Wide use in the chemical industy

- Solvent for dyes, e.g. in printing inks extractant
- Additive in polishes and cleaners
- Solubilizer in the textile industry
- Mobile phase in paper and thin layer chromatography
- Feedstock for the production of glycolethers (in reactions with ethylene or propylene oxide)
- Starting material for various butyl-monocarboxylates
- Feedstock for the production of flotation aids, e.g. butyl xanthate

Perfect as biofuel

- Low enthalpy of vapourization
- Low absorbance of water
- High energy density
- Octane rating 95
- Can be blended into conventional fuel from 0-100%

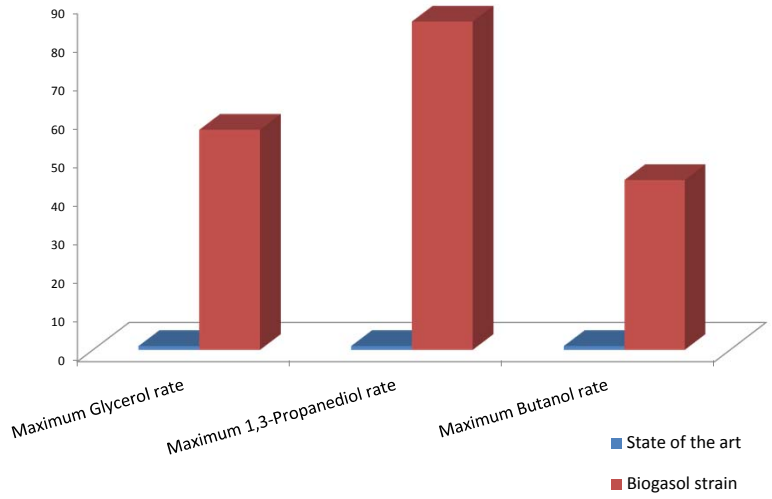
Microorganism

- A *Clostridium* strain was selected
- Natural producer of butanol, ethanol, butyrate, acetate, and 1,3-PDO
- Tolerates high concentrations of technical grade glycerol
- Was inhibited by crude glycerol

By chemical mutagenesis, selection, and evolutionary adaption

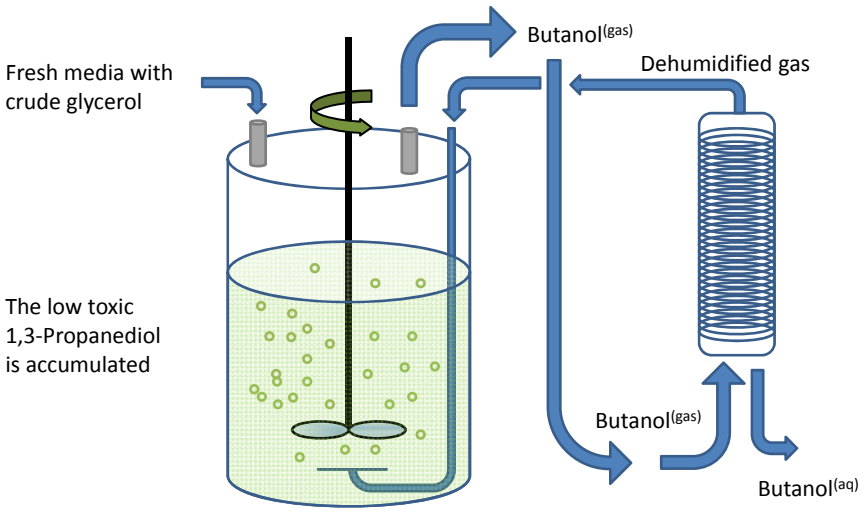
- Increased tolerance towards the crude glycerol
- Produces almost exclusively butanol and 1,3-PDO
- Elevated rates of glycerol consumption
- High production rates

Relative increase in rates



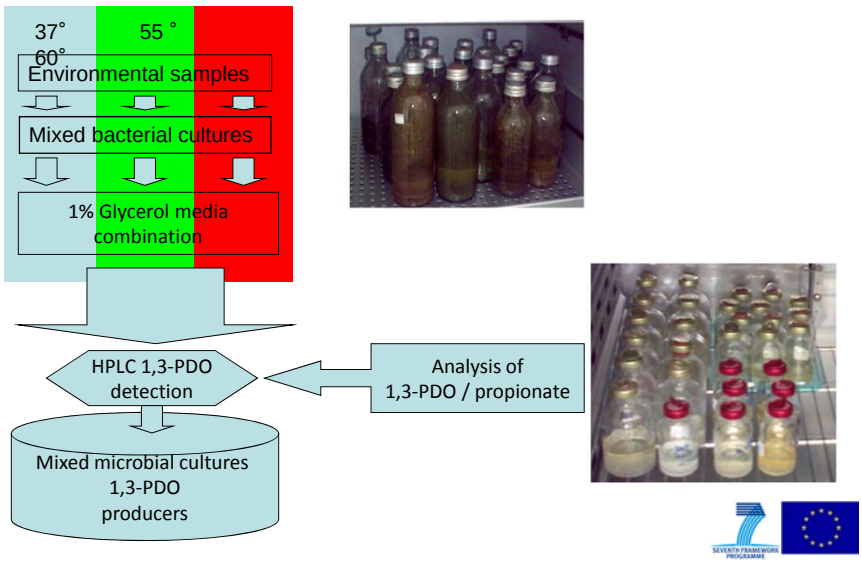
Two products are produced simultaneously

Butanol is removed *in situ*
1,3-Propanediol is accumulated in the fermentation broth

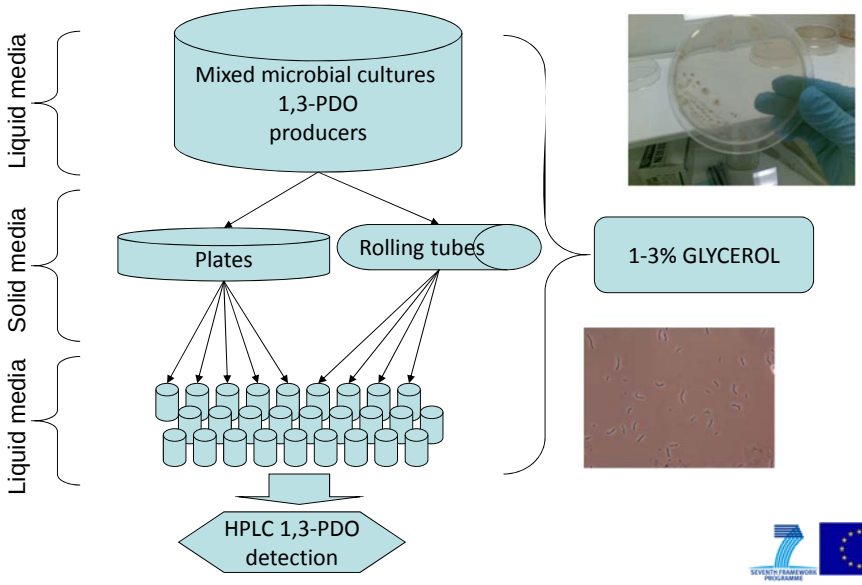


Production of green chemicals - A&A Biotechnology

Screening microbial cultures for production of 1,3-PDO



Isolation of new strains of glycerol fermenting bacteria producing alcohols or 1,3-PDO

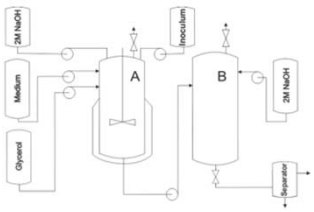


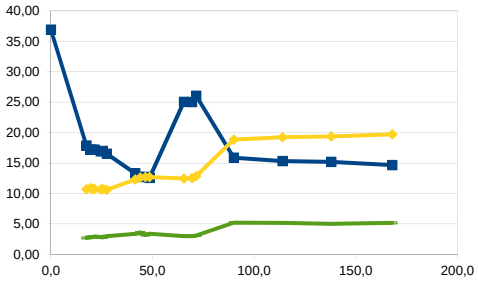
Characteristics of the 1,3-PDO fermentation

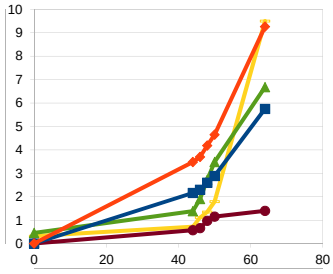
Fed-batch Fermentation

Results	Value
Total volume (liters)	29
Average efficiency PDO/Glycerol (mol/mol)	0.68
Highest temporary efficiency PDO/Glycerol (mol/mol)	0.96
Average butyrate conc. (g/l)	3.52
Time (h)	82
Total wet biomass (g), (g/l)	65, 2.13

2 stage model of 1,3- PDO continuous fermentation



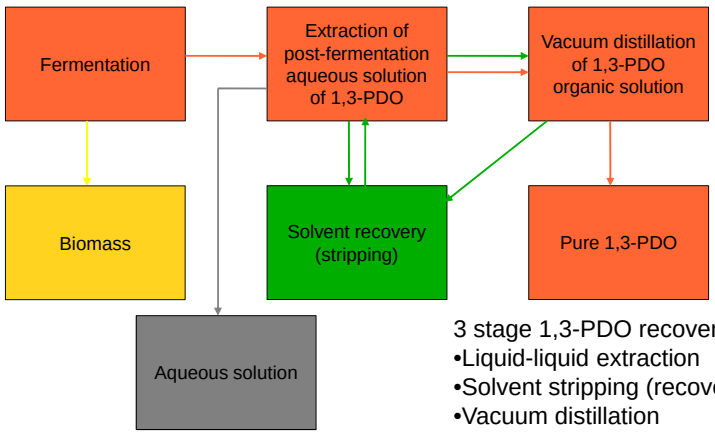




Process optimisation
Butanol production in the bioreactor batch fermentation system under pH control

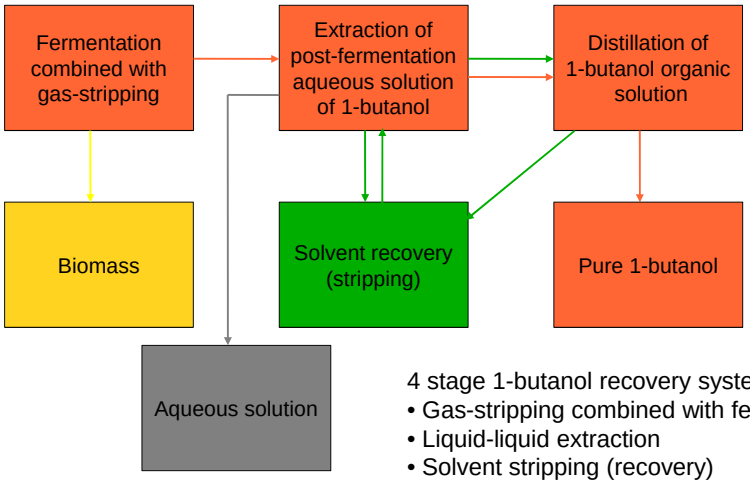
Product recovery – ProChimia Surfaces

Proposed 1,3-PDO recovery system



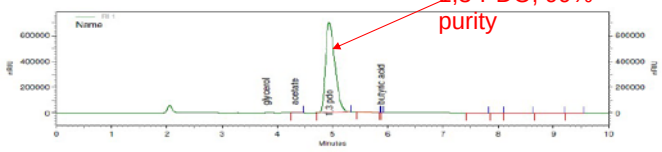
3 stage 1,3-PDO recovery system
- Liquid-liquid extraction
- Solvent stripping (recovery)
- Vacuum distillation

Proposed 1-butanol recovery system



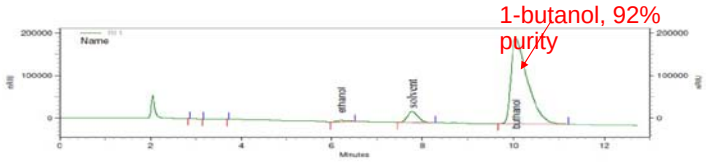
4 stage 1-butanol recovery system
- Gas-stripping combined with fermentation
- Liquid-liquid extraction
- Solvent stripping (recovery)
- Distillation

The lab-scale proof of concept has been demonstated for both proposed processes.



RI 1 Results

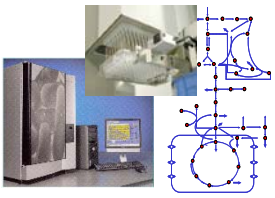
Name	Retention Time	Area	Concentration
glycerol	3.851	0	0.000 BDL
acetate	4.320	590251	0.127
1,3 pdo	4.937	830690470	109.730
butyric acid	5.875	0	0.000



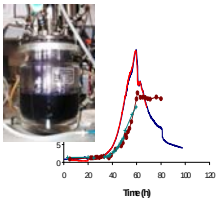
RI 1 Results

Name	Retention Time	Area	Concentration
glycerol	3.840	0	0.000 BDL
acetate	4.542	0	0.000 BDL
ethanol	6.212	5885913	1.603
buthanol	10.053	508953411	67.273
solvent	7.765	40670016	5.810

Timeline to pilot scale GLYFINERY



Isolation, screening and improvement



Process development
Product recovery

Process integration: pilot plant

March 2008 — March 2010 — March 2012

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www.glyfinery.net