Biorefining opportunities in conventional oil sector

Biorefinery Training Course. Biomass Valorization Congress

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Rubén Miravalles Gutiérrez. Refining, Marketing and LPG. Repsol R&D Division.

Agenda

- Introduction
- Biofuels today
- Biofuels in the future
- Other examples of integration in oil sector

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Introduction

- Main challenges to achieve a sustainable energy supply
  - Energy consumption is mainly based in fossil sources (coal, gas and crude oil)

    ⟶ increase participation of renewable energy
  - Reduce European energy dependence on external sources
  - Reduce greenhouse gases (GHG) emissions. Transport fuels has a great participation on GHG emissions

- European Directives promoting the use of bio-energy and affecting oil sector
  - EU Directive 2003/30/EC, promoting mandatory incorporation of biofuels in road transport fuels (5,75% energetic base in 2010)
  - Proposal for 2020: increase amount of biofuels from 5,75% to 10% (energetic base)
  - Fuel Quality Directive (2009/30/EC): obliges to reduce by 10% GHG between 2011 and 2020 (compared to emissions in 2010).

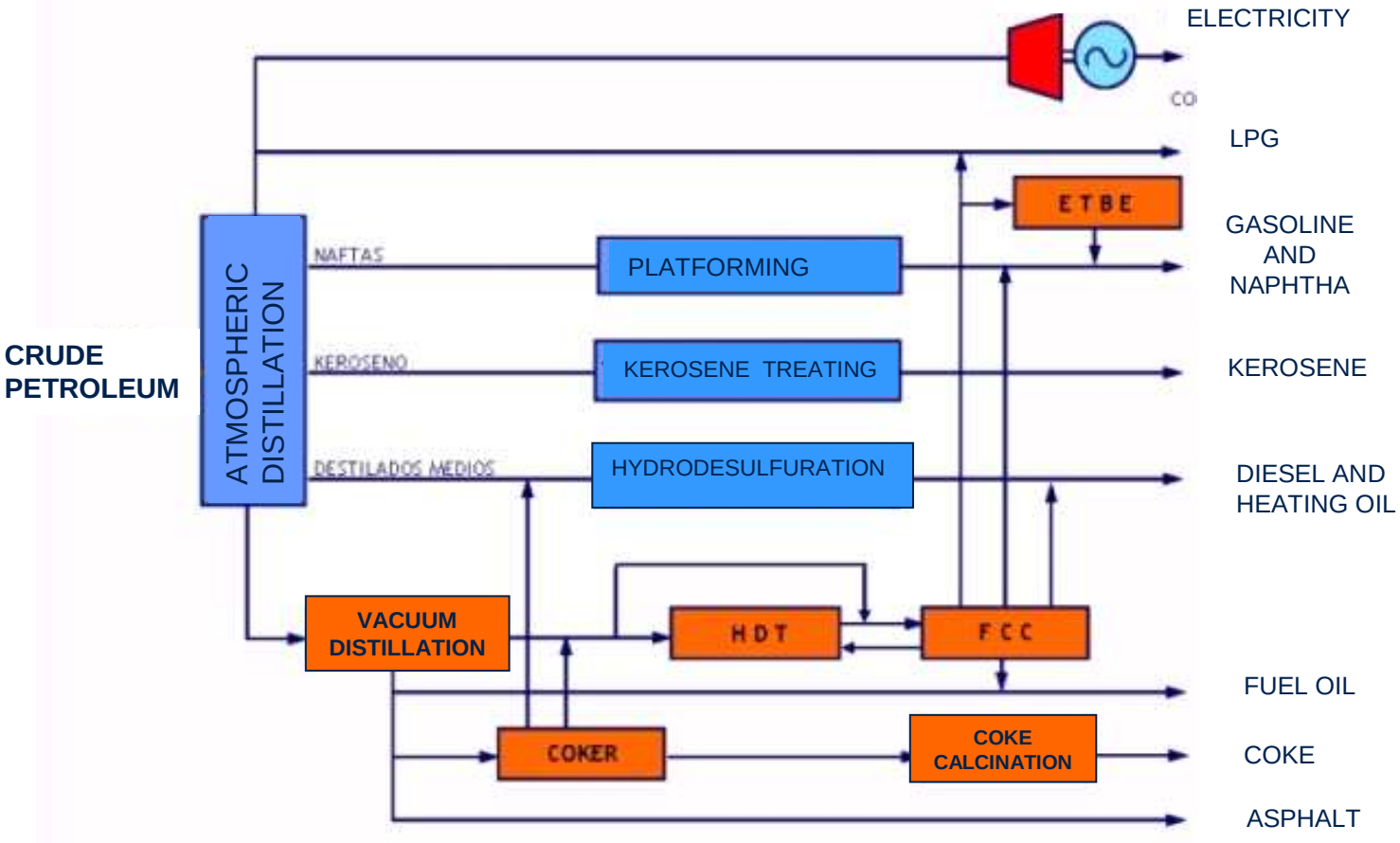
Introduction

- On the other hand, fuels must comply European quality standards….
  - EN-228 (gasoline) / EN-590 (diesel)
  - Some specifications in these standards limit the incorporation of high volumes of conventional biofuels (bioethanol and biodiesel):
    - EN-228: maximum vapour pressure, maximum oxygenated compounds and distillation curve in gasoline
    - EN-590: maximum 7%vol FAME in diesel
- … and biofuels must be compatible with existing distribution logistic system and current motors
- It is necessary to develop new biofuels as similar as possible to conventional ones, to achieve a higher participation

Introduction

- Conventional oil refinery: simplified scheme

  Refinery: production facility composed of several inter-connected processes to convert crude oil into heating and transport fuels and other products (lubricants, asphalts, coke, etc). Final products are a blend of several intermediate streams



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Biofuels today

- Biofuels used today: mainly 1st generation biofuels blended with gasoline and diesel.
  - Gasoline:
    - Direct route: blending of bio-EtOH (other alcohols / ethers also possible)
    - Indirect route: Integration of bio-EtOH etherification processes
  - Diesel:
    - Direct blending of biodiesel, mainly Fatty Acid Methyl Esters (FAME)
    - Trans-esterification is a well-known and easy process…. But there are possibilities for research and innovation

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- Introduction
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- Biofuels in the future: co-processing in refinery units
- Other examples of integration in oil sector

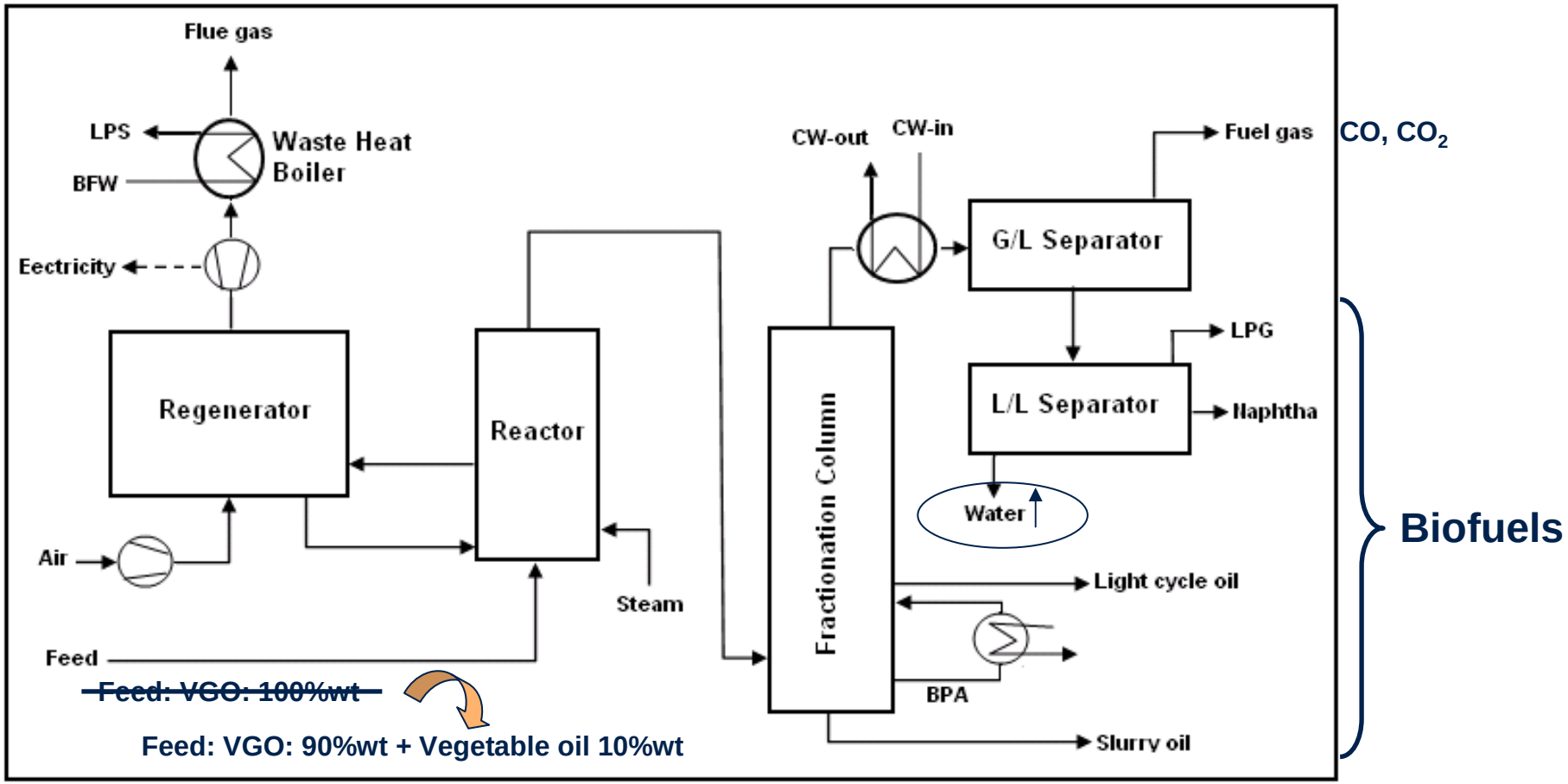
Biofuels in the future

- Co-processing of hydrocarbons from renewable sources in existing refinery units
  - Partial substitution of fossil by renewable feedstock
  - Potential feedstock: vegetable or algae oil, used kitchen oil, animal fats, pyrolysis oil, triterpenoids, etc
  - Oxygen content of renewable materials impact in the process
  - Process units: Fluid Catalytic Cracking (FCC) and HydroDeSulphurization (HDS)
  - Extensive R&D is on-going in this area. Repsol researches since 2006 in co-processing vegetable oil / animal fats in FCC and HDS
  - Alternative evaluated in BIOREF-INTEG project (funded by 7FP of European Union). For more info: www.bioref-integ.eu

Biofuels in the future

- Co-processing of vegetable oil in FCC

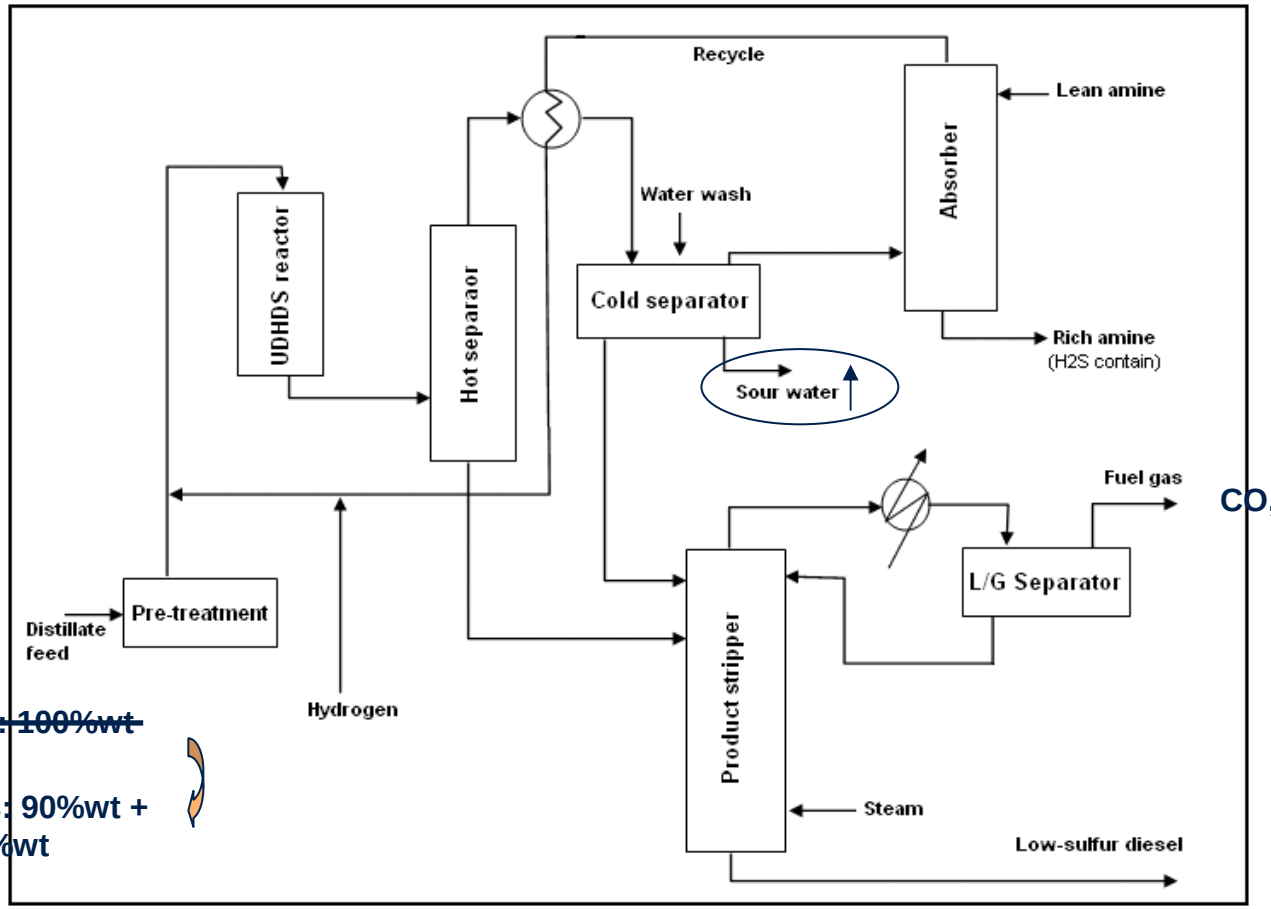
Objective: convert vacuum gasoil at low P (1-3 bar) and high T (490-550ºC) with an acid catalyst, into lighter molecules (LPG, naphtha, gasoil and heavy oil). By-products produced: fuel-gas, coke and H_2S.



Biofuels in the future

- Co-processing of vegetable oil in HDS

Objective: eliminate sulphur present in middle distillates (kerosene and diesel), using H_2 at high P, high T and a fix-bed catalyst.



~~Middle distillates: 100%wt~~

Middle distillates: 90%wt +
Vegetable oil 10%wt

Biofuels (HVO)

Biofuels in the future

- Co-processing of vegetable oil in FCC-HDS (technical issues)
  - Vegetable oil is cracked under the operating conditions of the unit.
  - Oxygen present in vegetable oil is converted to CO, CO_2 and H_2O.
    - Part of the feed go to non valuable products (impact in economics)
    - Slight increase in O&P costs due to the downstream processing of CO, CO_2 and H_2O
    - Higher H_2 consumption
  - Minimum amount of oxygen (ppm) in final products: biofuels produced are very similar to fossil fuels.
  - Some properties are enhanced (higher octane in gasoline / higher cetane and lower density in diesel).
  - Can be used in current motors without modifications, even at higher percentages

Biofuels in the future

- Co-processing of vegetable oil in FCC and HDS (economics)
  - Advantage: no need for additional investment (existing units are used)
  - Disadvantage: important increase in production costs: + 5 and 20% depending on feed cost and process. Economics in HDS is better than in FCC
  - Main factors affecting production cost are:
    - Differential cost between VGO and vegetable oil. Cost of production could be lower if “residual feedstock” is used (animal fat and used cooking oil)
    - Vegetable oil is partially cracked to non-valuable products: CO, CO_2 and water
    - Higher H_2 consumption in HDS

Biofuels in the future

- Co-processing of vegetable oil in FCC and HDS
  - Co-processing in HDS is preferred:
    - More focused in diesel production (deficit in Europe)
    - Increase in production cost is lower
  - Biofuels produced by this route should have tax benefits, as other biofuels, to compensate higher production costs
  - This alternative do not compete with current biofuels (complementary route):
    - Production of biodiesel (FAME) is more cost effective than co-processing vegetable oil in HDS unit, but limited by EN590
  - Extensive R&D program has allowed to go from laboratory scale to pilot plant and demonstration at industrial scale in 4 years:
    - Lab scale development started in 2006 (PIIBE project)
    - Pilot plant scale testing by Repsol 2008-2009 (internal project)
    - Two successful industrial trials in two different HDS units (Cartagena and Puertollano refineries): 2009-2010

Biofuels in the future

- Co-processing of other renewable feedstock in refinery
  - So far, co-processing focused in vegetable oil… but there are other alternatives:
  - Co-processing of bio-oil (pyrolysis oil)
    - Bio-oil is produced from lignocelluloses through thermal / catalytic pyrolysis
    - Advantages: lower cost compared with vegetable oil; produced from residual sources
    - Disadvantages: higher oxygen content = poorer quality (acidity, viscosity, Concarbon residue, stability, etc); technical feasibility to be demonstrated
    - Respol participates in HECABIO project (funded by ACENET-ERA): development of catalytic pyrolysis and upgrading of bio-oil in refineries

Biofuels in the future

- Co-processing of other renewable feedstock in refinery
  - Co-processing of hydrocarbons from laticifers
    - Laticifers produce hydrocarbons rich in triperpenoids
    - Advantages: lower oxygen content (higher C/O ratio), not competing with other sectors, selectivity to diesel (according to literature)
    - Disadvantages: technical feasibility to be demonstrated
    - Repsol participates in EULAFUEL project (Plant KBBE call): production and co-processing of latificer hydrocarbons in refinery units

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Other examples of integration

- Production of feedstock for biofuels: Jatropha Curcas project
  - Project with Latin-American partner to produce Jatropha Curcas under sustainable conditions in a tropical country
  - 25000 ha; Establishment of full plantation area by 2011/2012. Full production by 2015-2017
  - Full production chain: cultivation (partner), oil mill (partner), transport (partner-Repsol); oil refining (Repsol), oil processing: transesterification / co-processing by hydrogenation in refinery unit (Repsol)
  - Sustainability criteria will be assured and evaluated by an independent consultant

Other examples of integration

- Production of biomass and CO_2 capture: CO_2-funnels project
  - "Carbonic fertilization": combustion gases from refinery are routed to a greenhouse where biomass is produced
  - Objectives: study production of several short-cycle / high biomass-productivity species in semi-closed or open greenhouses (Mediterranean system) with carbonic fertilization. Study the effects of carbonic fertilization in yield and quality of the biomass
  - Spanish Consortium (Repsol, CNB, IBMCP, Synergia SL and Ciemat). Project funded by Plan-E (Spanish Ministry of Science and Innovation)

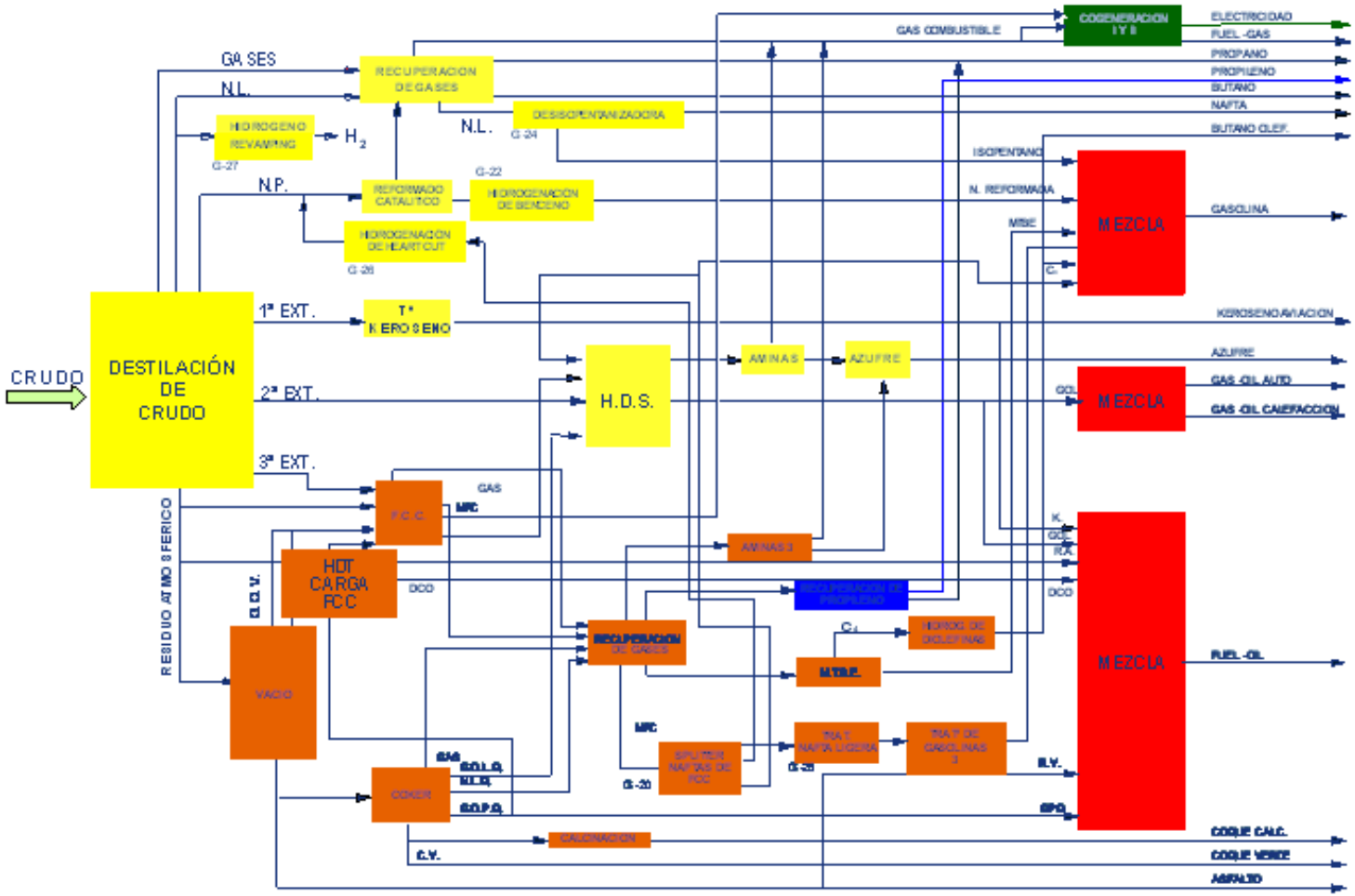
Other examples of integration

- Algae for biofuels and CO_2 capture
  - Algae as feedstock for biofuels: PIIBE project (2006-2009)
    - Project leader by Repsol. “Marine culture” work package in collaboration with Las Palmas University (Spain)
    - Microalgae selection, isolation and characterization of 44 algae strains. Innovative application of flow cytometry for micro-algae isolation
    - Development, patent an validation of a new photo-bioreactor
  - Algae for CO_2 capture: SOST-CO_2 project (2008-2011)
    - Spanish project leader by Air Liquide and funded by CENIT Program (Spanish Ministry of Science and Innovation)
    - Microalgae oil characterization
    - Comparison and optimization of culture systems and operating conditions
  - Development of new plastic materials with improved optical properties for algaeculture (photo-bioreactors)
    - Repsol is leader in Spain in plastics for greenhouse. We are applying our experience to develop FBR materials
  - Future project: cultivation of algae at demo scale, close to one of Repsol refineries


REPSOL
Inventemos el futuro

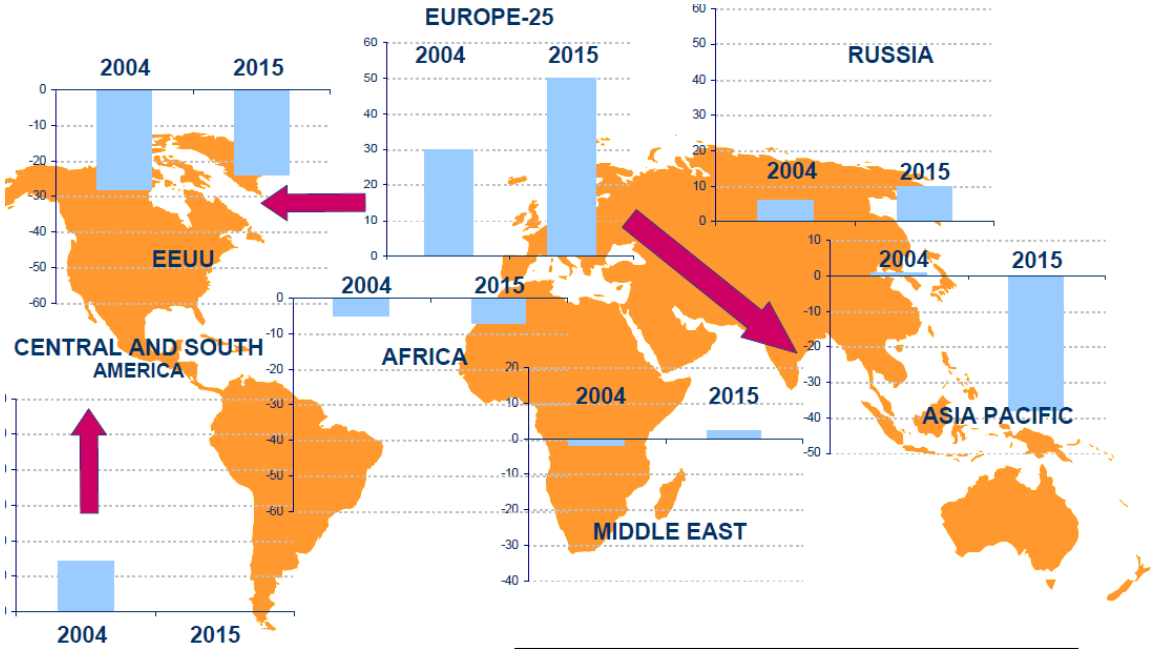
Introduction

- Conventional oil refinery: detailed scheme



Biofuels today

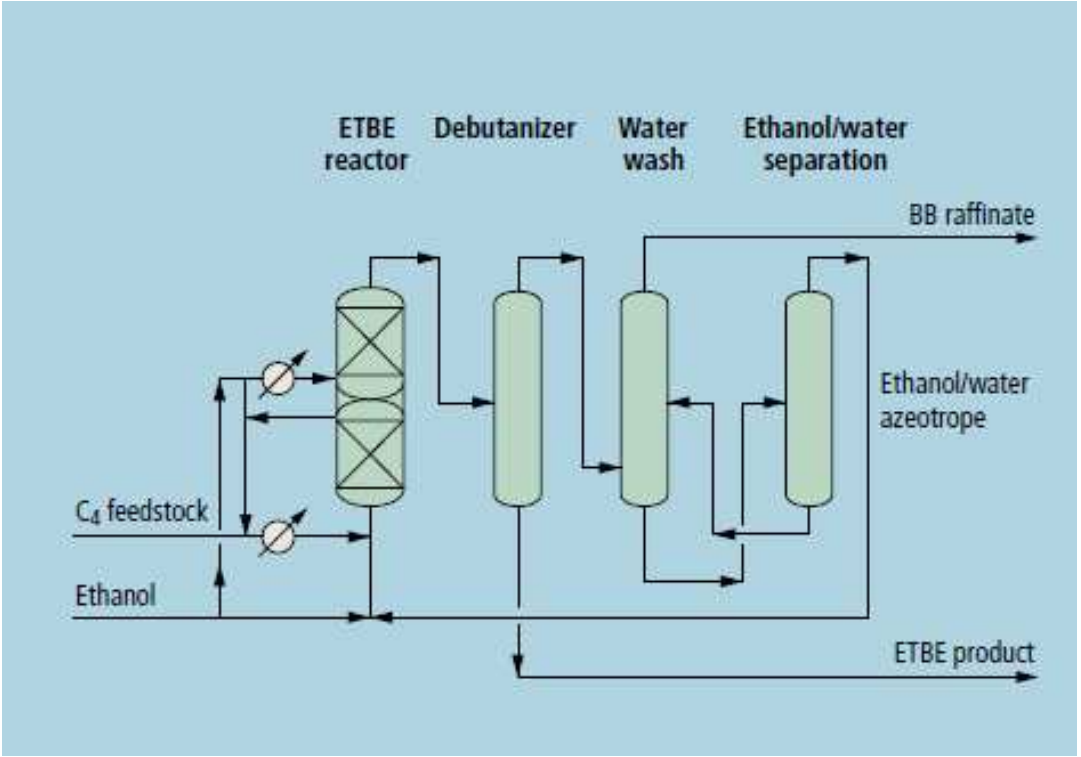
- BioEtOH direct blending in gasoline. Limitations:
  - Incompatibility with European quality standards limits it use. EN-228: max vapour pressure, max oxygenated compounds, max EtOH content and distillation curve
  - Europe surplus in gasoline production. Direct blending do not contribute to reduce imports



  - Requires a dedicated logistic system
  - For this reason, ETBE indirect route is preferred by oil sector

Biofuels today

- Integration of bio-EtOH in etherification processes:
  - Etherification process: production of high-octane ethers combining isobutene and alcohol (MeOH, EtOH). Process very common in oil refinery
  - Bio-EtOH can substitute fossil MeOH or EtOH as feedstock



Biofuels today

- Integration of bio-EtOH in etherification processes:
  - Repsol started in 2000 incorporating bio-ETBE in gasoline.
  - Transformation of fossil MeOH units (MTBE) to bio-EtOH units (bio-ETBE)
  - Advantages:
    - Easy implementation, no technical barriers
    - Many undesirable properties of bio-EtOH are avoided (vapor pressure)
    - No need for changes in distribution logistics
  - Disadvantages: limited by iso-butene availability

Biofuels today

- Biodiesel: PIIBE project (Research Project for the Impulse of Biodiesel)
  - Spanish project leader by Repsol and funded by CENIT Program (Spanish Ministry of Science and Innovation). 23 M€ budget, 15 partners, 23 R&D centers. 4 years: 2006-2009
  - Development of knowledge and technology along the whole biodiesel chain (raw materials – process – products)
  - Some achievements during the project:
    - Oil production from marine culture (Repsol)
    - One heterogeneous catalysis for FAEE production patented (Repsol)
    - Bio-lubricant developments: Increased Security Hydraulic Fluids based on fatty acids and water/glycerol. Four commercial products in the market (Repsol & partners)
    - Glycerol utilization: animal feed production, lubricants, diesel, petrochemicals (Repsol & partners)
    - Filtration: development of new filtration medias for FAME production process
    - Heating development: development of new burners for domestic boilers (Heating oil/FAME blends)
    - New feedstock: used kitchen oil for FAME production

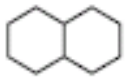
Biofuels today

- Biodiesel internal projects
  - Evaluation of alternative feedstock for biodiesel production: used kitchen oil, animal fats, jatropha and other non conventional oils
  - Use of high percentages biodiesel blends (>B7) in captive fleets
    - Light duty fleets: trial with B30 in a 100 vehicle fleet, 2 years. In collaboration with an European car manufacturer
    - Heavy duty fleets: trial with B15 / B30 in a 12 vehicle fleet, 1 year
    - Heavy duty fleets: trial with B30 in a 8 public transport buses fleet, 1 year. FAME from used kitchen oil
  - Optimization of Quality Standard EN-14214 (internal quality standars)
    - Total mono-glycerides limited to maximum 0,8%wt. Saturated Monoglycerides can provoke filter-plugging problems in diesel blends (even if TMG are below maximum)
    - Repsol has developed a method to detect filterability problems based in FBT after cold pretreatment
    - Repsol is researching in alternatives to reduce SMG during manufacturing (process optimization / filtering systems)

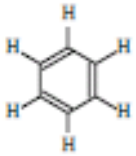
Biofuels in the future

Crude oil

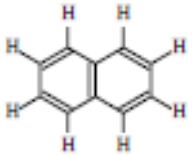
Cyclopentane



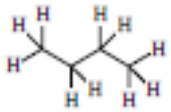
Decalin



Benzene

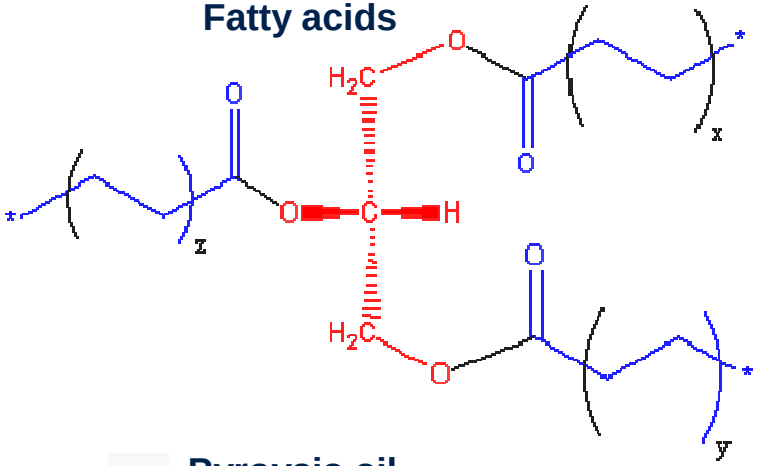


Naphthelene

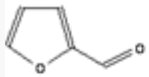


n-Butane

Fatty acids



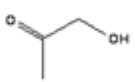
Pyroysis oil



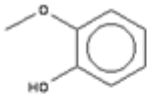
Furfural

Furan

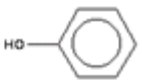
Acetic acid



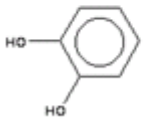
Acetol



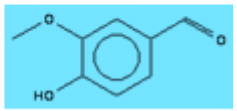
Guaiacol



Phenol

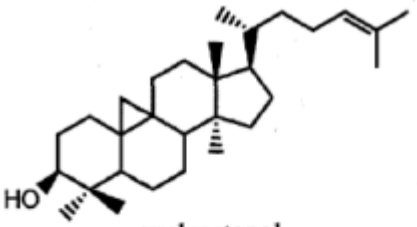


Catechol

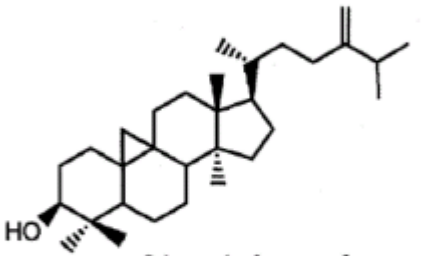


Vanillin

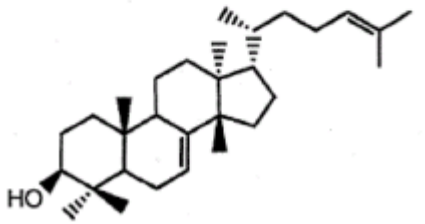
Triterpenoids



cycloartenol



24-methylenecycloartenol



butyrospermol