

THE CHALLENGE – BIODIESEL PRODUCTION
BIODIESEL DEMAND

The focus of many biodiesel producers is currently to get production facilities up and running as quickly as possible to take advantage of current demand, both consumer- and political- driven. As the process is fairly well known, well developed, and relatively simple to design, build and operate, rigorous simulation is only now generating strong interest. This has illuminated significant value-add opportunity in the optimization of the process(es), including energy usage & reactor conversion, for the many forward-looking biodiesel producers and process development groups.

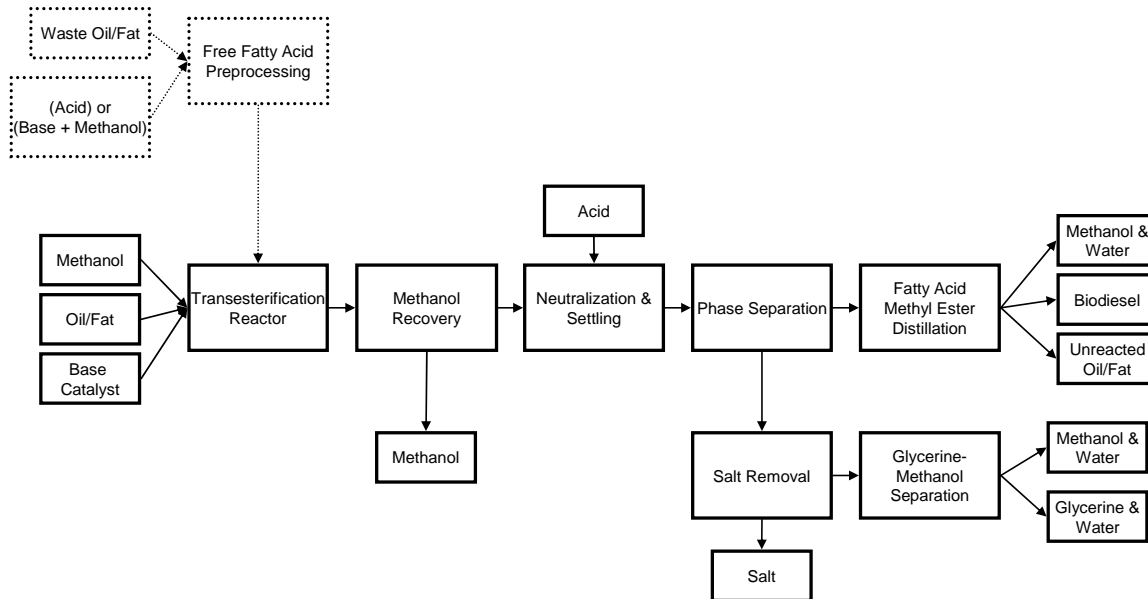
Biodiesel producers around the world are in a variety of stages of development: in early design stages, final equipment specification stages, or currently producing biodiesel. Decisions regarding what specific process to use, what feedstock to use (and how flexible the process can be to varying feedstocks), and what equipment to use can be made "offline" with rigorous models. A process flow diagram (PFD) with a heat and material balance in CHEMCAD allows for efficient process design to whatever level of optimization/fidelity is required.

As the biodiesel industry is in a state of flux, the five major forces affecting the entire Chemical Processing Industry (Increased Global Competition, Shorter Product Lifecycles, Rising Fuel/Feedstock Costs & Buyer Pressure, Reduced Engineering Staff, and Increased Regulation / Public Opinion) are beginning to drive producers to require optimized processes, high productivity (from tools and staff), better planning/scheduling/integration with business processes, and clean/green/sustainable facilities. CHEMCAD simulations are a starting point for addressing all of these issues now.

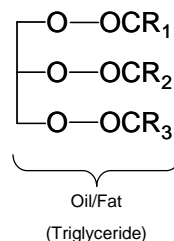
This document will outline the resources required and the advantages/disadvantages for various levels of CHEMCAD model fidelity.

BIODIESEL PRODUCTION PROCESS

A typical base-catalyzed (see REACTION section below for alternatives) process diagram is shown below. In this case, the preprocessing of Waste Oil is shown in dotted outline at the top left.


CHEMICAL COMPONENTS

Any vegetable oil or animal fat can be used as a feedstock for biodiesel production; as these are natural products, they are mixtures of several component oils and fats. These oils/fats are triglyceride molecules (glycerin esterified with three fatty acids). The $-R_x$ groups shown here varies according to the source of the oil/fat:



BIODIESEL IN CHEMCAD

For unused oils, such as soybean, palm, lard, etc., there is a typical assay showing the percentage of constituent fatty acids (from the -R_x groups above) making up the oil/fat. A table showing the weight percents of fatty acids contained in a number of common oils/fats is shown below:

Oil or fat type	Saturated									Mono unsaturated		Poly unsaturated	
	Caprylic Acid C8:0	Capric Acid C10:0	Lauric Acid C12:0	Myristic Acid C14:0	Palmitic Acid C16:0	Stearic Acid C18:0	Arachidic Acid C20:0	Behenic Acid C22:0	Lignoceric Acid C24:0	Oleic Acid C18:1	Erucic Acid C22:1	Linoleic Acid C18:2	Alpha Linolenic Acid C18:3
CHEMCAD ID	540	545	890	902	912	550	1534	NO	NO	549	NO	548	1529
CAS NO	124-07-2	334-48-5	143-07-7	544-63-8	57-10-3	57-11-4	506-30-9	112-85-6	557-59-5	112-80-1	112-86-7	60-33-3	463-40-1
M.E. CC ID	NO	1673	894	NO	NO	NO	NO	NO	NO	919	NO	NO	NO
M.E. CAS NO	111-11-5	110-42-9	111-82-0	124-10-7	112-39-0	112-61-8	1120-28-1	929-77-1	---	112-62-9	1120-34-9	112-63-0	301-00-8
Almond					7	2				69			17
Beef tallow		0.1	0.1	3.3	25.2	19.2				48.9		2.7	0.5
Butterfat	5.5	3	3.6	11.6	33.4	11.4				27.8		3.1	0.6
Canola				0.1	3.9	3.1				60.2	0.5	21.1	11.1
Cocoa Butter					25	38				32		3	
Coconut	8.3	6	46.7	18.3	9.2	2.9				6.9		1.7	
Cod Liver				8	17					22		5	
Corn					9.9	3.1				29.1		56.8	1.1
Cottonseed				0.8	22.9	3.1				18.5		54.2	0.5
Crambe					2.07	0.7	2.09	0.8	1.12	18.86	58.51	9	6.85
Flaxseed					3	7				21		16	53
Grapeseed					8	4				15		73	
H.O.safflower				0.34	5.46	1.75	0.23			79.36		12.86	
Lard		0.1	0.1	1.4	25.5	15.8				47.1		8.9	1.1
Linseed					4.92	2.41				19.7		18.03	54.94
Olive					11	3.6				75.3		9.5	0.6
Palm	0.1	0.1	0.9	1.3	43.9	4.9				39		9.5	0.3
Palm Kernel		4	48	16	8	3				15		2	
Palm Olein				1	37	4				46		11	
Peanut					10.4	8.9				47.1	0.2	32.9	0.5
Rapeseed					2.7	2.8				21.9	50.9	13.1	8.6
Safflower				0.1	6.6	3.3				14.4		75.5	0.1
Sesame					13.1	3.92				52.84		30.14	
Soybean				0.1	10.3	4.7				22.5		54.1	8.3
Sunflower				0.1	6	5.9				16		71.4	0.6
Sunola					3	4.4				88.2		4.3	0.1
Walnut					11	5				28		51	

Composition of various fats & oils.

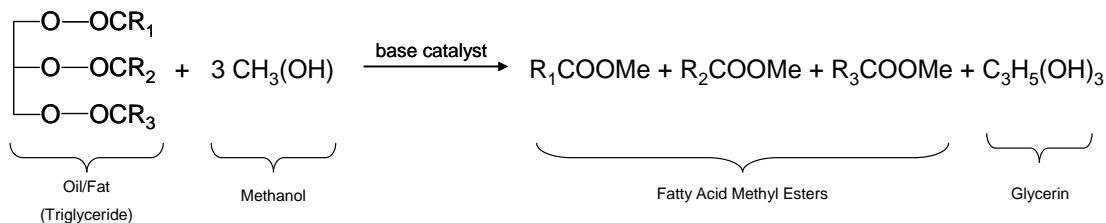
As can be seen in the table above, CHEMCAD's implementation of the DIPPR database provides users with most of the fatty acid compounds, but only a few of the methyl esters. Chemstations has access to physical properties of many of the methyl esters from literature sources, and will provide them when requested by customers so that user-added compounds can be added to biodiesel flowsheets.

When the oil has been used (waste oil), there are usually larger amounts of free fatty acids present than in virgin oils (due to the heat from cooking, for example). For biodiesel production, these free fatty acids must be removed with a base or pre-processed with acid esterification to esters before transesterification to prevent soap formation.

FATS/OILS TO BIODIESEL REACTION

The three basic methods of ester production from oils/fats are 1) base catalyzed transesterification, 2) acid catalyzed esterification, and 3) enzymatic catalysis. Each reaction has associated optimal operating parameters (T & P) and conversion, although much of the available literature emphasizes the base catalyzed route because it is claimed to be the most economical.

The overall base catalyzed reaction, for example is as follows:



The reaction progresses in three reversible steps: 1) the triglyceride reacts with the alcohol to form a diglyceride and a fatty acid ester, 2) the diglyceride reacts with the alcohol to form a monoglyceride and a fatty acid ester, and 3) the monoglyceride reacts with the alcohol to form glycerin and a fatty acid ester. For example, if palm oil, with at least 9 different fatty acid groups, is used, there could potentially be 729 different triglycerides, 81 different diglycerides, and 9 different monoglycerides present.

Based on the assay of any particular starting oil/fat, there will be an associated assay of fatty acid esters in the final biodiesel product. The type of alcohol used determines the type of esters formed (for example, if Methanol or Ethanol are used, then Methyl- or Ethyl- esters are formed).

THE SOLUTION – CHEMCAD SIMULATION

RIGOROUS METHOD

Requirements:

- ✓ Physical Properties of all oil/fat constituent components (TG's, DG's, MG's), fatty acids, and fatty acid ester products
- ✓ Full Kinetic parameters for all reactions (Arrhenius constants)
- ✓ Vapor-Liquid-Liquid BIPs for all component pairs in critical separations

Advantages:

- ✓ Easily compare plant performance for various/varying feedstocks
- ✓ Easily optimize both reaction and separation sections

Drawbacks:

- ✓ Mammoth amount of data required, much of which is unavailable in literature. Expensive measurement resources required.
- ✓ Simulation likely to be slow because of the large number of components and reactions, limiting real-time optimization opportunities

SHORTCUT METHOD

Requirements:

- ✓ Single fatty acid to represent oil/fat: Oleic acid is a major component of many vegetable oils. A common approach is to use triolein to represent the triglyceride form of oleic acid.
- ✓ Single fatty acid ester to represent biodiesel product: the fatty acid methyl ester (FAME) derivative(s) for the component used as vegetable oil. For example, if you assume that oleic acid is your fatty acid form (with triolein being the triglyceride), then methyl oleate (C19H36O2) can be used as your FAME.
- ✓ Vapor-Liquid-Liquid BIPs (or data to regress) for FAME/glycerine/methanol system
- ✓ Assumed conversion in stoichiometric, forced reaction. It is common to model the reaction as having 90%+ conversion of feedstock to biodiesel. Many users begin their model with this assumption, even if they plan to add kinetics later.

Advantages:

- ✓ Simple, quick-to-build heat and material balances
- ✓ No need to find data for all the constituent components: Using a single component allows a single transesterification reaction. Oleic acid (C18H34O2) is the major fatty acid in canola oil (Lawson, 1995). Triolein (C57H104O6) can be used to represent the triglyceride form of oleic acid, and is readily available for use in a process simulator. Triglycerides are the main component of vegetable oil (Zhang, 2003). Zhang observed that the diglyceride and monoglyceride form were only observed as intermediates, with high methanol to oil ratios.

Drawbacks:

- ✓ No ability to compare plant performance for various/varying feedstocks
- ✓ Low fidelity model; less ability to perform optimization and less ability to use real-time optimization

HYBRID METHOD

Requirements:

- ✓ Single and/or Condensed list of fatty acids to represent oil/fat. Canola oil, for example, could be represented as a blend of oleic acid, linoleic acid and linolenic acid.
- ✓ Condensed list of fatty acid esters to represent biodiesel product. Again, using the esters of the list chosen for fatty acids (Canola: methyl oleate, methyl linoleate, methyl linolenate)
- ✓ Condensed list of Vapor-Liquid-Liquid (V-L-L) BIP parameters for fatty acids, glycerin, and methanol
- ✓ Condensed list of kinetic parameters. Kinetics are available for several oils/fats from the literature for simplified, reversible reactions:
 - triglyceride (TG) + MeOH \leftrightarrow diglyceride (DG) + FAME
 - DG + MeOH \leftrightarrow monoglyceride (MG) + FAME
 - MG + MeOH \leftrightarrow glycerin + FAME

Advantages:

- ✓ Some ability to compare plant performance for various/varying feedstocks (requires either multiple flowsheet versions for different oils or insuring that separate TG, DG, MG, and kinetics are included for each potential oil/fat used)
- ✓ Better fidelity for separation units (distillation columns, settling/phase separation units)
- ✓ Optimization of both reaction and separation sections is possible
- ✓ Medium fidelity and faster simulation times give potential for real-time optimization solutions

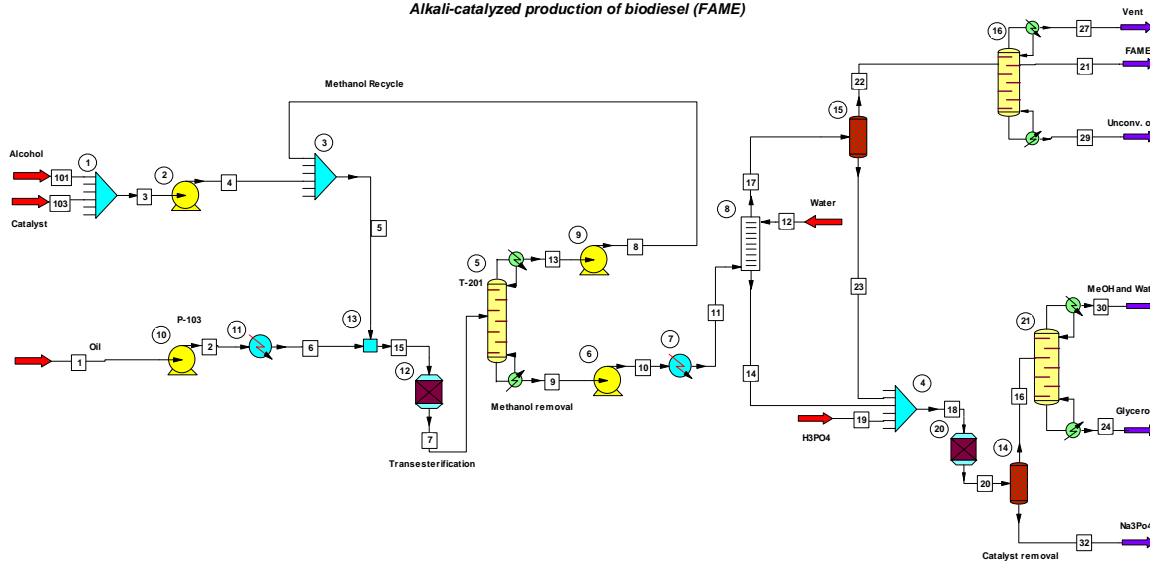
Drawbacks:

- ✓ More work to build the component list and kinetics for the reactor.
- ✓ More work to find and regress V-L-L data to BIPs

EXAMPLE (BASE CATALYZED SYSTEM) SIMULATION IN CHEMCAD

An overview of a "hybrid" type model in CHEMCAD follows:

Alkali-catalyzed production of biodiesel (FAME)



CHEMCAD Flowsheet

Stream No.	101	103	1	8	15	7	11	22
Name	Alcohol	Catalyst	Oil	Methanol Rec				
-- Overall --								
Mass flow kg/h	117.20	10.00	1050.00	111.65	1288.82	1288.84	1177.19	1060.14
Temp C	25.00	25.00	25.00	28.51	51.88	60.00	60.00	60.00
Pres kPa	100.00	100.00	100.00	400.00	400.00	400.00	110.00	110.00
Component mass %								
Methyl Oleate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Glycerol	0.00	0.00	0.00	0.00	0.00	8.05	8.81	0.00
Methanol	100.00	0.00	0.00	100.00	17.75	9.35	0.75	0.18
Calcium Oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Calcium Sulfate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phosphoric Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TriNa Phosphate	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Triacylglycerol	0.00	0.00	100.00	0.00	81.47	4.07	4.46	4.95
FAME	0.00	0.00	0.00	0.00	0.00	77.75	85.12	94.52
Sulfuric Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35
Sodium Hydroxide	0.00	100.00	0.00	0.00	0.78	0.78	0.85	0.00

Stream No.	18	27	21	23	30	24	32
Name		Vent	FAME		MeOH and Wat	Glycerol	Na3Po4
-- Overall --							
Mass flow kg/h	256.06	25.94	990.00	6.39	18.47	104.09	133.50
Temp C	47.05	214.27	214.27	60.00	38.78	112.00	60.00
Pres kPa	100.00	10.00	10.00	110.00	40.00	50.00	100.00
Component mass %							
Methyl Oleate	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Glycerol	40.52	0.00	0.00	0.00	0.07	99.66	0.00
Methanol	2.73	7.18	0.00	0.00	37.15	0.12	0.00
Calcium Oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Calcium Sulfate	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Phosphoric Acid	49.99	0.00	0.00	0.00	0.00	0.00	89.77
TriNa Phosphate	0.00	0.00	0.00	0.00	0.00	0.00	10.23
Triacylglycerol	0.00	0.45	0.87	0.00	0.00	0.00	0.00
FAME	0.00	78.27	99.12	0.00	0.01	0.00	0.00
Sulfuric Acid	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Water	2.86	14.10	0.00	0.00	62.77	0.22	0.00
Sodium Hydroxide	3.91	0.00	0.00	100.00	0.00	0.00	0.00

Key Stream Analysis

Customers may request the CHEMCAD files for this flowsheet along with flowsheets for 1) an acid catalyzed process, 2) the pretreatment of waste oil, and 3) "a process to produce biodiesel from waste-oil using hexane."

FREQUENTLY ASKED QUESTIONS (FAQ) FOR BIODIESEL SIMULATION IN CHEMCAD

I made new components for biodiesel / oil / glycerin. Why are the components flashing to vapor?

When you make new components in CHEMCAD, critical properties are predicted. The vapor pressure is predicted from these values with a rough correlation. It is not uncommon to have an unrealistic result for vapor pressure, particularly for the biodiesel.

To improve results, regress vapor pressure data for the components. Experimental vapor pressure should show a low vapor pressure curve for these components. Go to the Tools menu > Pure Regression to regress vapor pressure for the component.

If experimental data is not available, consider regressing hypothetical data which shows a low vapor pressure. This will prevent the component from flashing to vapor. Be sure that the hypothetical data is consistent with your normal boiling point. The vapor pressure vs. temperature curve of triolein may be useful as a reference.

What other properties are important for my new components?

Typical models involve distillation and flashes. The more important transport properties for user added chemicals are vapor pressure, liquid heat capacity, heat of vaporization, and vapor heat capacity. Density is useful for pump calculations. Thermal conductivity and liquid viscosity become important if you are using CCTHERM.

How do I model the settling unit or a wash?

The settling unit is typically a liquid liquid separator. You could use a flash unitop with three outlets for a liquid-liquid separation. If you are performing a water wash, you could use an extractive column with a small number of stages. Zhang uses an extractive column with 4 ideal stages to represent washing, followed by liquid-liquid flash units to represent the gravity settling.

What thermodynamics do I use?

This is a tricky question: thermodynamics can be very important for this model. Biodiesel, methanol, water, vegetable oil, and glycerin residue have non-ideal thermodynamics.

It's common to use a liquid – liquid extraction to separate the biodiesel from the glycerin. Your model must predict two liquid phases to perform this separation.

The base or acid catalyzed process may require electrolyte thermodynamics, for the neutralization and heats of solution.

It's common to use NRTL, UNIQUAC, or Modified UNIFAC for this process. Here are some best practices from our modeling experiences:

- ✓ Assign UNIFAC subgroups to the components you are using for Biodiesel, vegetable oil, and glycerin. This will allow a subgroup method to 'predict' VLE based on subgroups
- ✓ Use NRTL for the transesterification and methanol recovery section of the flowsheet. Use Modified UNIFAC for the liquid-liquid separation and the purification columns (evaporators).
- ✓ If you are going to use Electrolytes, you need to use NRTL for the entire flowsheet. Regress missing BIPS for the systems water-biodiesel, biodiesel-oil, water-oil, biodiesel-methanol, and biodiesel-glycerin
- ✓ Use methanol partitioning data from Chiu to benchmark the separation of methanol at the extraction unit
- ✓ Use experimental data to regress more accurate BIPs (tools > BIP regression) where available.

How do I model the neutralization?

The electrolyte package only shows neutralization if you have true species electrolytes activated. If you are not using true species electrolytes on your flowsheet, it is common to use an isothermal stoichiometric reactor to perform the neutralization. Turn off electrolytes at this unitop if you are using apparent species electrolytes. The heat duty of this unitop will be meaningless; perform the neutralization in true species electrolytes if you need more rigorous heat duty calculation.

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Expertise



The Company

- P & I Design Ltd was established in 1978 to provide services to the process industry
- Located in the North East of England we are ideally located for National and International work
- Our multi-disciplined engineering workforce can provide:

Process Engineering

- General process engineering design with specific expertise in batch process and waste management industries
- Process Modelling and Simulation

Process Software

- Sole UK and Ireland agents for internationally renowned simulation software suite CHEMCAD
- Process engineers toolkit - design aids for process design
- Lihou HAZOP reporting software

Safety & Environmental Legislation

- Expertise in the preparation of Health & Safety reports
- Risk assessment studies

Instrument, Electrical and Control Engineering

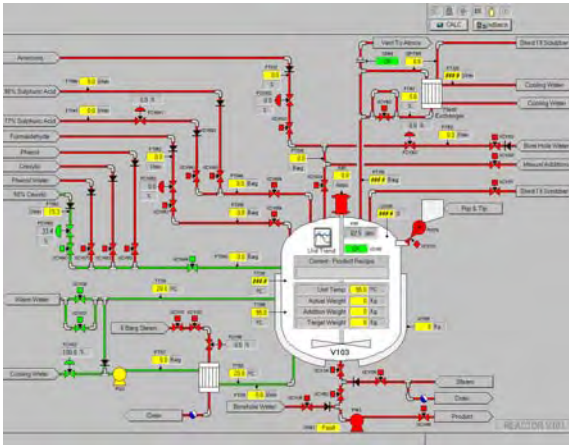
- Instrumentation and electrical system design
- Control systems, including PLC, DCS & SCADA programming
- Safety Instrument System Design to IEC 61508 / IEC 61511
- Calibration and Commissioning

Computer Services

- IT systems and networks design and support
- CAD drawing facilities
- Data base development, project management and engineering software

Quality Assurance

- P & I Design's quality assurance system and procedures are approved to ISO 9001:2000



Scope of Services

Project Management

- Contract management and planning
- Tender documents and tender evaluation

Process Engineering

- Feasibility studies
- Consent planning
- Conceptual and detailed design
- Process Modelling and Dynamic Simulation
- Relief and Blowdown System design and analysis

Safety, Health and Environmental Legislation

- COMAH safety case studies
- HAZID, HAZOP and LOPA Risk Assessments
- IPPC Applications, BAT and waste minimisation
- DSEAR – Explosive Atmospheres Directive (ATEX) and Chemical Agents Directive (CAD) studies

Instrument/Electrical Engineering

- Conceptual and detailed design
- Control systems design
- Calibration and testing facilities
- Hazardous area classification
- Safety Instrument System design

Information Technology

- Design of industrial networking solutions
- Design of business networking solutions using wired & wireless Ethernet
- Remote Access solutions
- Server & Client applications utilising latest Server & Client technology
- Bespoke application design
- Experts in Microsoft's Small Business Server 2000 and 2003

Legal

- Expert Witness

Site Services

- Supervision of installation, testing and commissioning services
- Site Survey by COMPEX Certified Engineer

Training & Seminars

- Risk Assessment, LOPA and ATEX
- CHEMCAD software suite
- Batch Processing



Experience



Industry Sectors:

Fine Chemicals

- Batch Reactor Control
- Gas Scrubbing
- Distillation
- Separation & Drying
- Hazardous Material Handling
- Utility Systems

Services

- Waste Management and Recycling
- High Integrity Power Supply Control Systems
- Waste Site Remote Management
- Government Agency Consultancy

Storage and Materials Handling

- LPG Storage and Distribution
- Petroleum & Chemicals Storage Terminals
- Pipeline Transfer Systems
- Road & Rail Tanker Loading Facilities
- Terminal Automation

Environment Technology

- Conceptual Studies
- Process Design
- Specific Experience
- Regulatory Advice

Information Technology

- Industrial Networking
- Consultancy and System Solutions
- Commercial and Small Business

Clients

- Since incorporation in 1978 we have provided a service to many national and international companies, both large and small. Providing independent consultancy and design services and undertaking turnkey projects



