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BlueDiesel

Technology and Production Overview

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BLUEDIESEL
TECHNOLOGY AND PRODUCTION OVERVIEW

CONTENTS

Appendices

BLUEDIESEL
TECHNOLOGY AND PRODUCTION OVERVIEW

1. EXECUTIVE SUMMARY

BlueDiesel's (Pty Ltd) proof-of-concept, biodiesel pilot plant has undergone a series of process testing and evaluation throughout 2006 and 2007. These tests and assessments have occurred under varying conditions and with a wide range of feedstocks, and their results are detailed in this report.

This report includes a basic biodiesel production summary, an explanation of the key measures required to evaluate biodiesel quality, a synopsis of BlueDiesel's innovative process and its advantages, a detailed analysis of the biodiesel process results that have been generated using BlueDiesel's pilot plant, current limitations and issues of the pilot plant, and an explanation of the measures required to overcome these issues in future plant designs.

1.1. Biodiesel Production Background

The biodiesel production process can be broken into four main stages: reaction, separation, methanol recovery, and washing. In the reaction stage a fatty acid triglyceride (oil or fat) is reacted with a primary alcohol (usually methanol, sometimes ethanol) in the presence of a catalyst to produce fatty acid methyl ester (FAME or biodiesel) and glycerine. This is called a transesterification reaction. The next stage is the separation of biodiesel and glycerine. Biodiesel is non-polar and less dense than water, glycerine is polar and denser than water – this means that either gravity or centrifugal separation can be used. An excess of alcohol is used in the first stage to push the reaction to completion, so after separation the excess alcohol is then recovered. The final stage is the 'washing' of the biodiesel to remove any remaining impurities, such as residual methanol, glycerine, or catalyst.

A vast majority of biodiesel processes use a base catalyst for the transesterification reaction. This has the advantage of being many times faster than an acid catalyst, but has the disadvantage of being intolerant of free fatty acids (FFAs) in the feedstock. FFAs are produced by various mechanisms. FFA content is dependent on the feedstock and generally higher FFA content feedstocks are lower in price than low FFA feedstocks. FFAs inhibit a base catalysed transesterification reaction by reacting with the base to form soap and water. This removes the catalyst from the reaction and also encourages the formation of more FFA. In order to overcome this issue pre-treatment may be required to reduce the FFA content to an acceptable level. There are several processes used to reduce FFA content.

Biodiesel has a number of international quality standards, the three primary ones being EN 14212, ASTM D 6751, and the Australian Biodiesel Standard (ABS). The key measures of biodiesel quality that are process dependent are:

1. **Ester content** – the measure of how far the transesterification reaction has progressed. The ABS and EN standards specify a minimum ester content of 96.5% (i.e. less than 3.5% unreacted oil or other material). Low results for ester content generally indicate poor quality fuel which may cause many problems including corrosion, filter and injector blockages, and poor combustion.
2. **Free and total glycerine** – another measure of the completeness of the transesterification reaction and also a measure of quality of washing of biodiesel. The ABS and EN standards set a maximum on the free and total glycerine of 0.02% and 0.25% by mass respectively. The

EN standard has additional specific limits on mono-, di-, and triglycerides (bound glycerine) which are summed with the free glycerine to give total glycerine. The ASTM standard only specifies a maximum total glycerine content of 0.24% by mass. High results on these tests indicate a fuel that may have problems with formation of monoglyceride precipitates, phase separation (which can lead to corrosion or blockages), or poor combustion.

3. **Methanol content and flash point** – a measure of the safety of the biodiesel fuel. The ABS and EN standards set a maximum level of methanol of 0.2% by mass and a minimum flash point of 120°C (the ASTM standard only specifies a minimum flash point of 130°C). These are essentially related as it is primarily the methanol content that governs the flash point. A high methanol content, and corresponding low flash point, indicates a fuel which cannot claim to give significant safety benefits (fossil diesel has a minimum flash point of 55°C). Very high methanol content can exacerbate other problems with phase separation and corrosion.
4. **Water and other contamination** – a measure of the cleanliness of the fuel. The ABS and ASTM standards specify a maximum water and sediment content of 0.05% by volume. The EN standard specifies a maximum water content of 500ppm. The ABS and EN standards specify a maximum filtered contamination content of 24ppm. Excess water or contamination can lead to problems with phase separation, corrosion, and filter and injector blockages.

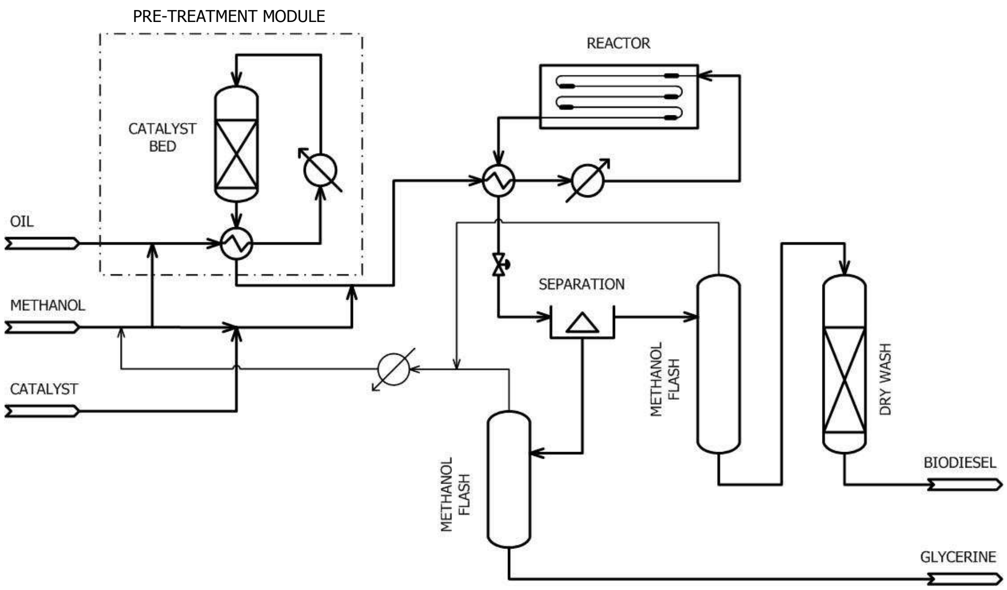
There are other measures of biodiesel quality that are specifically related to the feedstock. Most important of these are cloud point and oxidation stability. **Cloud point** is the temperature at which the fuel begins to solidify. This indicates the minimum ambient temperature at which the fuel may be used before filter blockage is likely to occur. **Oxidation stability** is a measure of fuel life in storage. A low oxidation stability result indicates a fuel that is more likely to break down whilst in storage, creating polymers or peroxides that can lead to corrosion and filter or injector blockages.

2. BLUEDIESEL PROCESS AND TECHNOLOGY

BlueDiesel has a proprietary biodiesel production process. The technology has been tested in a proof-of-concept, pilot scale plant (production capacity 1 million litres per year). The pilot plant comprises a solid-acid catalysed free fatty acid (FFA) reducing pre-treatment module, a base catalysed high pressure high temperature continuous tubular reactor, centrifugal phase separation, vacuum flash methanol recovery for biodiesel and glycerine, and a solid resin adsorption ‘wash’ for biodiesel.

BlueDiesel’s proprietary technology specifically relates to the tubular reactor and the associated Pressure Reduction Device. The FFA pre-treatment module is not BlueDiesel’s technology but the application of the technology to biodiesel is generally considered novel. The remaining process technologies are generally considered within the realms of standard process design, and have been selected for low capital costs and ease of operation.

BLUEDIESEL
TECHNOLOGY AND PRODUCTION OVERVIEW



The key aspects of our technology are:

1. The transesterification reaction is carried out at **high temperature and pressure**. The high temperature speeds up the reaction via three mechanisms: increased chemical activity, increased mutual solubility of reagents and improved mixing due to reduced viscosities of the materials.
2. The reaction proceeds continuously in a **tubular reactor**. We have overcome the issues with stratification of immiscible materials in the reactor by using patented mixing devices throughout the reactor length.
3. We use a special patented **Pressure Reduction Device** (PRD) at the outlet of the reactor in order to avoid irreversible emulsification of the products (biodiesel and glycerine) when the pressure is dropped to atmospheric level.
4. The pre-treatment module uses a **solid acid catalyst**, directly converting FFA to biodiesel. Use of a solid catalyst means that the complexity and capital cost of equipment associated with the dosing and neutralizing liquid acid catalyst is removed.

The benefits of this technology are:

1. The **capital cost of the plant is considerably reduced**. Based on published costs for current conventional plants and our own cost estimates, the CAPEX savings should exceed 50%.
2. The **size of the plant is reduced**, with container-sized shipping options for commercial scale plants possible.

3. The **operating costs are reduced**, due to decreased power requirements. A conventional plant uses more power in mixing alone than our plant would use all-up. This is because in a conventional plant mixing occurs at lower temperatures, and the viscosity of the oils used in the process is several times higher.
4. The **inventory of liquids in the reactor is lower**, by two orders of magnitude. This is an important safety feature, since the liquids are highly flammable.

Our process addresses the key quality aspects in the following ways:

1. High pressure, high temperature continuous tubular reactor – results in **high ester content** (98%+) in a single stage, which means there is only one stage of reagent dosing and one stage of separation, vastly reducing process control complexity. Separation efficiency is improved due to the **low glyceride** levels.
2. Centrifugal separation – results in **high efficiency separation** which reduces 'washing' requirements. Centrifugal separation can also deal with **phosphatide gums** which are present in some feedstocks. The gums form an insoluble intermediate phase between the biodiesel and glycerine phases which can't be removed using normal gravity separation but can be ejected using a solids discharge type centrifuge.
3. Vacuum flash methanol recovery – removes **methanol** to specification levels in one step **without using water**. This removes the need for complex and energy intensive water treatment equipment.
4. Solid resin adsorption 'wash' – removes **trace glycerine and other contaminants** without using water.

3. BLUEDIESEL PROCESS RESULTS

The BlueDiesel pilot plant has been used to test the production of biodiesel from various feedstocks. This has both proven the technology and highlighted some of the issues of dealing with various feedstocks. The plant has been tested on canola oil, mustard oil, palm olein, coconut oil, and tallow (see Appendix A).

3.1. Canola oil

Canola oil is seen as the premium oil for producing biodiesel because of its large production volumes, ease of processing and the properties of the resulting biodiesel. The oil is obtained by expeller pressing (hot or cold) or solvent extraction from canola seed. Cold pressed oil has a low phosphatide gum content, and a slightly higher unsaturated fatty acid content than hot pressed or solvent extracted oil. The low gum content means that the oil does not need to be degummed prior to use in conventional biodiesel processes. Cold pressed oil is usually more expensive, because the recovery of oil contained in the seed is somewhat lower than with other processes. The higher unsaturated fatty acid content means that the biodiesel has a slightly lower cloud point but has a lower oxidation stability and cetane number. Hot pressed oil has a higher gum content and higher saturated oil content, and usually needs to be degummed before the biodiesel process.

In our testing we have processed both hot and cold pressed canola oils. The hot pressed canola oil had been partially degummed but the quality of the oil was variable and we did encounter accumulation of the insoluble gums in the separation stage. Both oils were easy to process and gave good ester content results.

As expected, biodiesel produced from cold pressed canola oil had a relatively low oxidation stability. Untreated, the biodiesel had an oxidation stability of 5.6 hours (minimum acceptable is 6.0 hours). With the addition of IRGASTAB™ antioxidant the oxidation stability was increased to 7.8 hours.

3.2. Mustard oil

Mustard oil is an emerging feedstock for biodiesel. Although related to canola, it is not as widely grown as canola as the oil and meal are not particularly suitable for human or animal consumption. The oil is obtained in the same manner as canola oil, namely expeller pressing (hot or cold) or solvent extraction from mustard seed. The same issues with gums are present with mustard oil. An additional problem is that the oil has been tested showing approximately 50 ppm of sulphur which means that the resulting biodiesel is likely to have a sulphur content of greater than the specification level of 10 ppm.

In our testing we have processed hot pressed, partially degummed mustard oil. The quality of the oil was variable and we did encounter accumulation of the insoluble gums in the separation stage. The oil was very easy to process and gave good overall results. The ester content was consistently high (greater than 98%). The tested sulphur content of mustard oil biodiesel was 15 ppm. The biodiesel also exhibited an increased cloud point when compared with canola oil, but is still suitable for most temperate climates.

3.3. Palm olein

Palm oil is one of the largest volume edible oils produced world wide. It is seen as a lower cost feedstock but there are downsides to the resulting biodiesel. Palm oil is produced by expeller pressing or solvent extraction from the ‘flesh’ of the oil palm fruit. The resulting crude oil is split into two components by cooling the oil and separating the liquid from the solid. The liquid fraction is called palm olein and the solid fraction called palm stearin. Both of these products are usually further processed by refining (removal of FFA), bleaching (removal of colorants) and deodorising (known as RBD oil). Crude palm oils have a FFA content of approximately 5%.

In our testing we have processed RBD palm olein. The palm olein was solid at room temperature and needed heated storage and heat tracing on the oil supply lines. Palm olein processed easily and gave consistently good overall results. The oxidation stability was also very high due to the large proportion of saturated fatty acids in the palm olein. The downside of the high content of saturated fatty acids is the cloud point was tested as 12°C, making it unsuitable to be used neat throughout the year in most climates.

Another issue was the high level of contaminants present in the tested sample, although this may be due to high melting point fractions depositing on the filter media used to determine the mass of the contaminants in the sample.

3.4. Coconut oil

Coconut oil is produced in large quantities for cooking oil, cosmetics and other related products. Coconut oil is produced by expeller pressing or solvent extraction from copra – the edible ‘meat’ of a coconut. Coconut oil is also generally further processed by refining, bleaching and deodorising (RBD). Crude coconut oil has a FFA content of approximately 5%. Coconut oil is high in short-chain saturated fatty acids, which means that the oil itself has a high melting point but the resulting biodiesel does not. The short-chain fatty acids also present an issue in the testing of ester content. Currently, the ABS and EN standards only count fatty acid methyl esters (FAMEs) from 14 carbons to 24 carbons in length. Coconut oil has only approximately 40% of its fatty acids in this range, with fatty acids as short as 6 carbons in length. This leads to artificially low results for ester content, when tested by the method prescribed in the ABS and EN standards. Coconut biodiesel is therefore not used in the countries mandating these standards, however it is entirely suitable as diesel engine fuel and is used in other countries (notably the Phillipines) which do not mandate such standards.

Coconut oil esters are used in non-fuel applications (solvents and feedstock for other oleochemicals), and may command a premium when sold for such uses instead of as fuel.

In our testing we have processed both crude and RBD coconut oil. The coconut oil was solid at room temperature and needed heated storage and heat tracing on the oil supply lines and pre-treatment module. The crude coconut oil processed well in our pre-treatment module, with the FFA content being reduced from 5% to less than 0.4%. The treated and RBD coconut oils processed very well in the main plant, giving consistent good conversion results.

3.5. Tallow

Tallow is seen as a low cost feedstock for biodiesel. Tallow is produced by rendering animal carcasses and offal. Tallow can be further processed by bleaching which removes the colorants and particulates present in crude tallow. Tallow is further graded according to its FFA content, with high FFA tallow being considerably cheaper than low FFA tallow.

In our testing we have processed both bleached and un-bleached tallow high FFA tallow. We discontinued using un-bleached tallow because particulates present in this grade are filtered by and accumulate in the pre-treatment catalyst bed. Tallow is solid at room temperature, having a melting point of at least 40°C, and needs steam-heated storage and heat tracing to the tallow supply lines and the pre-treatment module. Many issues had to be overcome with dealing with such a high melting point feedstock.

The tallow processed well in the pre-treatment module once optimum operating conditions were determined. The FFA content was reduced from 3% to less than 0.4%. The tallow processed well in the main plant, giving consistent good overall results. The ester content of the tallow biodiesel had to be determined using a modified method to the one in the ABS and EN standards because the standard method uses an internal standard (C17 FAME) which is also present in tallow biodiesel.

Tallow has a high content of long-chain saturated fatty acids which result in a very high cloud point (approximately 14°C), making it unsuitable to be used neat throughout the year in most climates. This also causes problems when blending with fossil diesel as the temperature must be elevated to prevent the biodiesel crystallizing. Other unsaponifiable fatty materials present in trace amounts in tallow, such as sterols, can cause issues with blending tallow biodiesel with fossil diesel.

4. CONCLUSION

In conclusion, BlueDiesel's testing to date has conceptually proven our proprietary technology, being the high pressure high temperature tubular reactor, and the PRD. We have also proven the application of the FFA pre-treatment technology to the production of biodiesel.

There are clear advantages that BlueDiesel's technology has over conventional biodiesel processes, specifically the lower initial capital costs, process cost benefits, and the ability to produce biodiesel from both refined and low FFA feedstocks with detailed tests for verification.

The strength of BlueDiesel's technology gives offer to a range of commercial opportunities both as a producer of biodiesel and/or as a manufacturer of biodiesel plants, as well as providing the option of licensing the technology in various regions to potential/existing biodiesel producers.

Appendix A – Summary of Feedstocks Processed

Oil	Canola oil		Mustard oil	Palm olein	Coconut oil		Tallow	
Extraction / treatment	Hot pressed	Cold pressed	Hot pressed	RBD	Crude	RBD	Un-bleached	Bleached
Pre-treatment required? (FFA %)	No	No	No	No	Yes (5%)	No	Yes (3%)	Yes (3%)
Results								
Ester content	~ 98% (5)	97.9%	98.2%	98.5%	-	34.8% (1)	-	97.9%
Total glycerine	-	0.13%	0.07%	0.07%	-	-	-	0.11%
Methanol content / flash point	-	0.04% / 154.4°C	0.17% / 147.5°C	0.06% / 158.5°C	-	-	-	-
Total contamination	-	20.9 ppm	17.7 ppm	52.0 ppm	-	-	-	-
Cloud point	-2°C (3)	-5°C	3°C	12°C	12°C (3)	12°C (3)	14°C (3)	14°C (3)
Oxidation stability	3 – 9 hrs (3)	7.8 hrs (2)	6.1 hrs	15.4 hrs	(4)	(4)	1 hr (3)	1 hr (3)
Processing Issues								
Gums present	Yes	No	Yes	No	No	No	No	No
Feedstock solid at room temp.	No	No	No	Yes	Yes	Yes	Yes	Yes
Particulates	No	No	No	No	No	No	Yes	No

Notes:

1. The ABS standard only measures esters in the C14-C24 range while coconut oil has a majority of esters in the C6-C14 range. The ester content in the C8-C24 range was 91.5%. This does not count the C6 esters present.

2. The oxidation stability was improved by adding a proprietary antioxidant. The untreated oxidation stability was 5.6 hours.
3. Results obtained from literature.
4. Coconut oil has only 5% saturated fatty acids so the oxidation stability is expected to be in excess of 20 hours.
5. Not tested in an independent laboratory.

Appendix B – Example of Test Results

Results relate only to sample received. The sample was tested and the following results were obtained.

Client's Name	BlueDiesel	Sample No	BLUE060712C
Product	Canola Biodiesel	Client Ref. No.	070607-1900-x
Source	-	Date Sampled	various
Container	1L x 1	Date Received	12/06/2007
Remarks	-	Date Reported	13/09/2007

Parameter	Method	Specification Australian Standard		Result	Units
		Min	Max		
Free glycerine	ASTM D6584		0.02	0.01	% mass
Total glycerine	ASTM D6584		0.25	0.13	% mass
Total contamination	EN 12662		24	20.9	mg/kg
Acid number	ASTM D664		0.8	0.62	mgKOH/g
Water content	ISO 12937		0.05	0.018	mg/kg
Oxidation stability**	EN 14112	6		7.8	Hours
Ester Content	EN 14103	96.5		97.9	% Mass
Linolenic Methyl Ester Content	EN 14103		12	11.8	% Mass
Total Sulphur	ISO 20846		10	1.0	mg/kg
Phosphorus	EN 14107		10	0.1	mg/kg
Group 1 metals (Na+K)	EN 14108		5	0.9	mg/kg
Group 2 metals (Mg+Ca)	EN 14538		5	0.1	mg/kg
Methanol content*	EN 14110		0.2	0.04	% Mass
Flash Point*	ASTM D93	120		154.4	ºC
Cold Filter Plugging Point	EN 116			-9	ºC
Ash content	ASTM D874		0.02	0.002	% Mass
Copper corrosion (3hrs, 50ºC)	ASTM D130		1	1A	Degree of corrosion
Iodine number	EN 14111		120	119	g I/100g
Carbon residue on 100% distillation	ISO 10370		0.05	0.02	% Mass
Density at 15ºC	ISO 3675	860	890	882.1	kg/m^3
Viscosity at 40ºC	ASTM D445	3.5	5	4.13	mm^2/s
Distillation T90	ASTM D1160		360	359.4	ºC
Cetane Number^	ASTM D613	51		51.0	

* Test done on resample 070607-1900-2 18/06/07

** Test done on resample 070607-1900-5 07/09/07 plus 500ppm IRGASTAB B100 antioxidant prepared in the ASG laboratory

^ Test preformed by ASG Germany