VFA as a Route to Renewable Transport Fuel

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ABSTRACT

Declining petroleum resources, increased demand by emerging economies, and political and environmental concerns about fossil fuels are driving the search for new sources of renewable fuels. Currently the only sustainable source of organic carbon is biomass, but biofuel production must target idle and marginal land and use of wastes and residues so that it does not contribute to rising food prices that adversely affect the poorest. In order to achieve such a vision, the FP7 collaborative research project SUPRABIO aims to deliver novel unit operations that can be integrated into economic biorefinery options for the sustainable production of biofuels. Volatile fatty acids (VFA) offer a possible route for such an option. VFA may be economically produced on relatively small-scale from different waste sources and locations to allow a distributed production system to be realised. To make VFA suitable for use as a transport fuel, they need to be converted to alcohols or esters ideally through hydrogenation. The hydrogen source for such a conversion process may be readily provided by the fermentation of up to15% of the VFA. The remaining challenges include more efficient substrate hydrolysis to achieve greater VFA yield; effective VFA recovery and low cost catalysts as well as more innovative reactor designs for economical fuel production.

KEY WORDS

Second generation biofuel; sludge management; technology assessment; environment; resource recycling; sustainability.

1. INTRODUCTION

Declining petroleum resources, increased demand for petroleum by emerging economies, political and environmental concerns about fossil fuels are driving our society to search for new sources of fuels, particularly for transportation purposes. Currently the only sustainable source of organic carbon is biomass, which is abundant throughout the world. EU Renewable Energy Directive requires Member States to meet Renewable Transport Fuel Obligation (RTFO) target of 5% by 2010. However, this has been met mostly through the import of so-called First Generation Biofuels at a considerable social cost. In 2008 Secretary of State for Transport Ruth Kelly invited the Renewable Fuels Agency to undertake a review of the Indirect Effects of Biofuels (The Gallagher Review, 2008). According to Gallagher there is probably sufficient land for food, feed and biofuels, but biofuel production must target idle and marginal land and use of wastes and residues. Presently biofuels contribute to rising food prices that adversely affect the poorest. Current evidence suggests that the proposed EU biofuels target for 2020 of 10% by energy is unlikely to be met sustainably and the introduction of biofuels should therefore be slowed while we improve our understanding of indirect land use change and effective systems are implemented to manage risks. Specific incentives must also be provided to stimulate advanced technology development.

The EU is currently supporting a number of research projects that aim to deliver more efficient biorefinery technologies under the European Commission’s Sustainable Biorefineries Programme (FP7-2009-BIOREFINERY-CP). For example SUPRABIO, a large-scale collaborative research project involving 16 European organisations (SUPRABIO, 2011). Its overall objective of is research, development and demonstration of novel intensified unit operations that can be integrated into economic and sustainable biorefinery options for the production of second-generation biofuels, intermediates and high value products, together with assessment of the outcomes to inform and enable sustainable implementation.

Under SUPRABIO Volatile fatty acids (VFA) are considered as a possible route for second-generation biofuels. In this paper we aim to provide a detailed description of this novel concept, how it may be implemented in practice and a review of the foreseeable challenges.

2. THE VFA FUEL CONCEPT

VFA are carboxylic acids with a carbon chain of six carbons or fewer. They are typically created through fermentation in the digestive tracks of herbivores and omnivores. Examples include acetate, propionate and butyrate. The natural degradation of organic matter under anaerobic condition is a complex chain of biochemical reactions effected by several types of micro-organisms that require little or no oxygen. Industrial digesters commonly operate at 35°C and a minimum of 12 days retention time to provide optimum condition for the growth of the microbes that produce the necessary enzymes for all the biochemical reactions. The process occurs in three distinct steps, namely: *Hydrolysis, Acidogenesis* and *Methanogenesis*. The overall biochemical reactions may be summarised as follows:

$$\mathbf{C_6H_{13}O_5 + xH_2O \rightarrow COOH\text{-}(CH_2)_n\text{-}CH_3 \rightarrow 4CH_4 + 2CO_2}$$

$$\text{Substrate + water} \rightarrow \text{volatile fatty acids} \rightarrow \text{methane + carbon dioxide}$$

By reducing the bioreactor minimum retention time to less than 6 days and maintaining a low pH, it is possible to suppress the methanogenic reactions and allow VFA to be recovered as the products of choice. To make VFA suitable for use as a transport fuel, they need to be converted to alcohols or esters. These can be typically manufactured by the hydrogenation of VFA, as illustrated below:

Alcohols: $\mathbf{RCOOH + 2H_2 \rightarrow RCH_2OH + H_2O}$ Equation 1
Esters: $\mathbf{2RCOOH + H_2 \rightarrow RCOOCR + 2H_2O}$ Equation 2

3. FUEL MANUFACTURE

3.1 VFA feed stocks

In the EU there are many waste streams, which are suitable for VFA manufacture. Some of the most promising applications are considered here.

3.1.1 Sewage sludge

Sludge production and disposal are entering a period of dramatic change, driven mainly by EC legislation. Over the last 20 years, implementation of the Urban Wastewater Treatment Directive has resulted in at least 50% increase in the volume of sludge being produced in Europe while disposal of wastes has become very restrictive. For example, sludge disposal to sea had become illegal and disposal to landfill has also become virtually impossible with various regulatory amendments pursuant to the Landfill Directive since 2002. Further increases in sludge production can be expected due to implementation of the Water Framework Directive (Directive 2000/60/EC of the European Parliament). Per capita sludge production is approximately 20kg per year. Sludge is an excellent source of nutrients (N and P) for crop production and organics for energy (VFA) production. Tables 1 provides an illustration of the gross composition sewage sludge.

Table 1 - Gross composition sewage sludge (% w/w)

	Protein	Carbohydrate	Fibres	Lipids
Primary sludge				
Mean values	19.77	24.37	22.17	9.53
Secondary sludge				
Mean values	40.43	26.27	0.59	1.51

Although currently there are more than 36,000 anaerobic digesters (AD) in operation in Europe, they only provide sufficient capacity for treating about 45% of the sludge generated from wastewater treatment.

3.1.2 Organic farm wastes

Energy recovery is becoming increasingly important for agricultural wastes. Energy can be recovered directly through burning agricultural waste products, or indirectly through the collection of by-products, for example, methane from anaerobic digestion (AD). A number of promising options for such wastes have been presented in a report by the Mass Balance Programme (2002). However, European countries have different approaches to agricultural waste recycling due to geographical influences, different agricultural practices and energy policies. Some of the issues involved can be seen in relation to the use of AD across Europe. Denmark, where agriculture and energy policy have been proactive in the development of AD, is seen as the market leader in centralised AD of agricultural wastes. Similarly, special incentives for farmers have led to the rapid growth of AD in Germany, which has more than 2500 farm-scale AD plants and a few large centralised AD plants (2005). Throughout the rest of Europe there has been limited implementation of large-scale AD facilities. Policy in the UK favours anaerobic digestion on environmental and energy grounds. However, the cost of anaerobic-digestion technologies restricts widespread implementation. Table 2 shows a list of possible agricultural waste streams that may be utilised for VFA production.

Table 2 - Possible agricultural waste streams that may be utilised for VFA production.

FRESH MANURE	Nitrogen	Phosphorus	Potassium	Calcium	Magnesium	Organic matter	Moisture content
	(N)	(P_2O_5)	(K_2O)	(Ca)	(Mg)		
	%	%	%	%	%	%	%
Cattle	0.5	0.3	0.5	0.3	0.1	16.7	81.3
Sheep	0.9	0.5	0.8	0.2	0.3	30.7	64.8
Poultry	0.9	0.5	0.8	0.4	02	30.7	64.8
Horse	0.5	0.3	0.6	0.3	0.12	7.0	68.8
Pig	0.6	0.5	0.4	0.2	0.03	15.5	77.6

Research by the University of Reading (2011) suggests that there is an estimated 200 million tonnes undiluted excreta produced annually in UK. Approximately 60% of this arises from grazing livestock, which is voided straight to grassland. The remaining 80 million tonnes are collected from buildings for storage and spreading. Of the collected manure, 50% (40 million tonnes) are in the form of slurries (Cattle and Pig). For large farms, or for farms where disposal of livestock waste is a serious problem (for example, pig farms without sufficient associated land for spreading), anaerobic digestion could be very attractive, but a concerted strategy is required for its introduction.

Farm slurries are therefore of particular interest because they have excellent potential for VFA production and could make a significant contribution to the energy supply for transport.

3.1.3 Other organic waste streams

There are wide ranges of organic industrial waste materials that can be used for VFA production. Potential feedstock from industrial waste sources includes:

- Food/beverage industry
- Starch/sugar industry
- Dairies
- Cosmetic industry
- Fish oil and fish processing residues

The UK, for example, produces between 16-18 million tonnes of food waste annually, of which 8.3 million tonnes is household food waste. Currently, over 8 million tonnes of food and drink wastes (from all sources) are sent to landfill of which 4.5 million is from households (Auty et al, 2010).

3.2 Alternative use of organic resources

AD is a popular technology for biowaste management due to two major benefits: renewable biogas production and residue can be used as fertilisers. However, it comes at a high cost. AD technology has significant capital and operational cost requirements due to the slow process kinetics and the need to transport and handle large waste and digestate volumes.

The biogas generated by AD has relatively low value compared to another forms of energy. The prices of fuels paid by UK industry (2009-10) suggest that diesel (gas oil) is almost 3X more valuable than gas per unit of energy (Table 3).

Table 3 - Prices of fuels paid by UK industry (2009-10)

Average All consumers	Pence per kWh
Coal	0.86
Heavy fuel oil	3.72
Gas oil	4.32
Electricity	6.66
Gas	1.67

Source: Department of Energy and Climate Change (2011)

In terms of application, as a form of energy, biogas also has a number of serious drawbacks. Firstly, raw biogas is considered to be a dirty fuel with a high level of H_2S that requires costly clean up before it could be used (for example in CHP engines for electricity generation). Second, the gas is not easily transportable and mostly has to be used at the point of production. Fugitive emissions due to leakage often account for 2-4% CH_4 loss which gives rise to a significant greenhouse gas contribution.

VFA on the other hand have none of the mentioned issues. Once VFA is generated from the fermentation process, it can be recovered and concentrated to facilitate transportation and storage. This also offers more flexibility for the downstream processing of the VFA intermediate. Table 4 shows a comparison of some key impacts between the two methods of energy production.

Table 4 - Impact analysis of VFA route and biogas route

Impacts	VFA route	biogas route
Capital requirements	Low	High

Transport cost	Low	High
Value of product	High	Low
Carbon footprint	Low	High
Biofuel contribution	High	Low

3.3 Production of VFA intermediates

The production of the VFA intermediates is one of the key steps in the manufacture of the new biofuel. Possible production schemes for VFA from the different types of wastes are shown below:

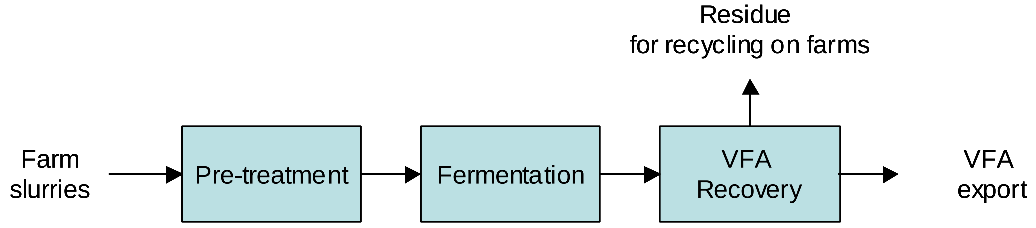

Figure 1 - Farm slurry treatment process

A farm-based VFA production system is likely to be simple and small-scale. Figure 1 shows the concept of a farm-based VFA production system where the pre-treatment comprises of basic screening of the gross solids for equipment protection. Fermentation may be carried out at 35°C and 6-day retention time in insulated glass-lined steel tanks. The VFA recovery may be potentially achieved by conventional membrane and adsorption processes. The residue, highly disinfected by the acid fermentation may be recycled locally returning valuable nutrients and organic matter to the soil.

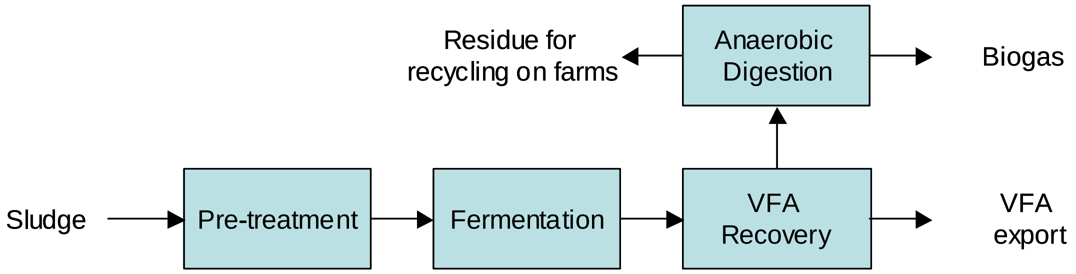

Figure 2 - Sludge treatment WwTW

A similar albeit larger VFA production system may be used on sewage works for sludge treatment. However, biological sludge is notoriously difficult to break down and that successful VFA production hinges on an effective pre-treatment step, which is further explored in the section below. Many sewage works in Europe already employ digesters which do not become redundant with the advent of VFA fermentation. Instead, they provide the added flexibility that enables operators to manage and balance the biogas production for on-site energy demand and VFA for export (Figure 2).

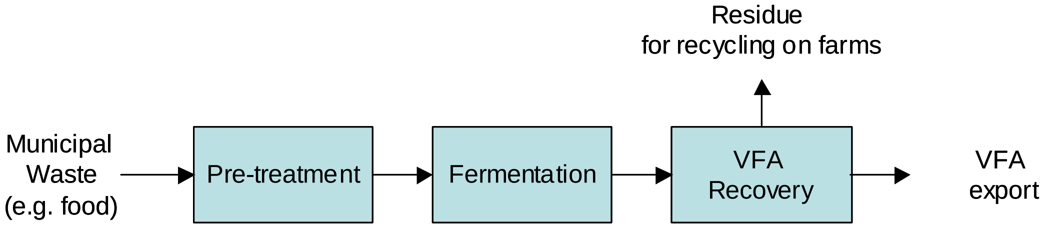

Figure 3 - Municipal waste treatment

The VFA production concept for food waste is again similar to the farm-based system. In this case, however, pre-treatment may have to include high temperature treatment to comply with the Animal By-product Regulations in addition to screening and macerations of the gross solids.

3.4 Production of hydrogen

Currently over 90% of the hydrogen used in industry originates from fossil fuels, with 50% from natural gas. Clearly, this is not sustainable longer term. In recent years, there has been a surge in interest in fermentation as a route for hydrogen production. The main advantage of hydrogen fermentation is the fact that it does not require glucose as substrate (Kapdan and Kargi, 2006). Hydrogen fermentation is dependent on organic acids as substrate for photo-fermentation with acetate, propionate and butyrate being the most important organic acids. The conversion may be illustrated as follows:

$$\mathbf{CH_3COOH + 2\ H_2O \rightarrow 4\ H_2 + 2\ CO_2} \qquad \text{Equation 3}$$

For alcohol production, up to 15% of the VFA need to be bio-transformed to hydrogen for the subsequent chemical conversion process. Ester production is 50% more efficient in hydrogen usage. Esters are good energy carriers, often used the basis of bio-diesel although they have a tendency to undergo hydrolysis, particularly under an alkaline condition.

3.5 Alcohol and/or ester production

The organisation of the biofuel manufacture posses the number of interesting challenges. According to Gomez and Guest (2004) there are now 22 Centralized AD facilities (CAD) operating in Denmark with digestion capacities ranging from 540m^3 to 6,900m^3 and daily capacities ranging from 50-500 tonnes of feedstock per day. Such schemes are limited by the logistics of moving large volumes of wastes to and fro between farms and the central facilities with the high economical, social and environmental costs that entail.

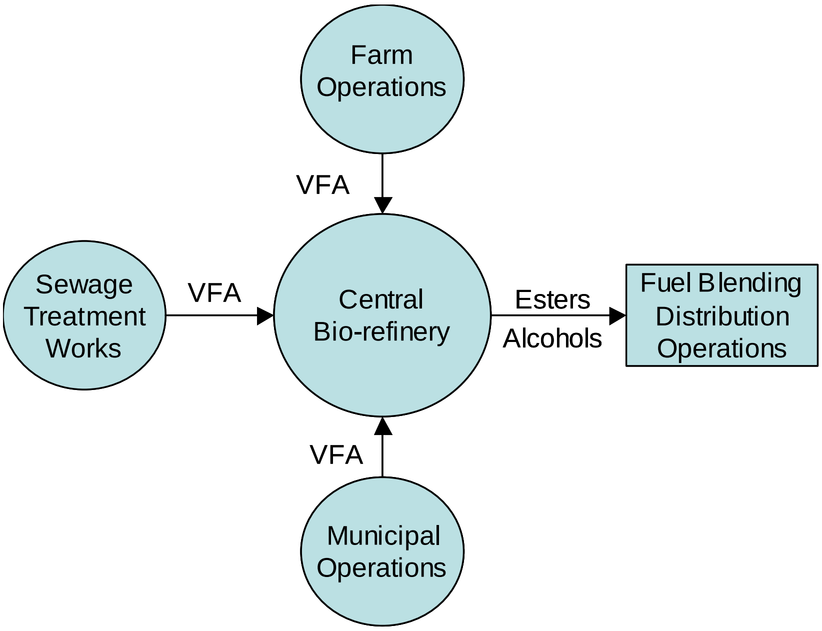

Figure 4 – Alcohol and/or ester production

The fact that VFA may be economically produced on relatively small-scale from different sources and locations allows a distributed production system to be realised. A centralised biorefinery may be conveniently located on a large sewage works, for example, to take advantage of local VFA production as well as the existing infrastructure such as roads, wastewater treatment and power supply. A distributed biofuel production system based on the VFA route is illustrated by Figure 4.

4. TECHNOLOGY CHALLENGES

4.1 Pre-treatment technologies

Many substrates, waste activated sludge in particularly, are only slowly biodegradeable. Hydrolysis is often the rate-limiting step in the overall VFA production process. Pre-treatment is the key to maximising yield and rate of the fermentation process. There are large numbers of technology options with varying degree of effectiveness for substrate pre-treatment. Many of these technologies are well proven with many full-scale sites in operation around the world. Table 5 below provides a summary of some of the better-known pre-treatment techniques.

Table 5 - Common technologies available for advanced fermentation

Technology	**Type**	**Temp (ºC)**	**Pressure (bar)**	**Sites**	**Reference**	**Commercial**
Acid phase	Biological	35-42	Atmospheric	<10	Wild,R. and Bjorn, A., 2009	Various
EH & EEH	Biological	42-55	Atmospheric	>10	Riches, S. et al., 2008	Monsal
Biothelys	Thermal	165	8-10	<10	Mountford,L., 2009	Veolia
Cambi THP	Thermal	165-170	8	>20	Riches, S. et al., 2008	Cambi
Ultrasonic	Acoustic	Ambient	Atmospheric	>10	Edgington, R. and Thompson, A., 2007	Sonico & Others
Cellruptor	Pressure /CO2	Ambient	5-10	<10	Spooner,J. et al., 2007	Eco-solids
Crown system	Shear	Ambient	12	<20	Froud, C. and Weber, R., 2007	Biogest
Grinding	Shear	Ambient	Atmospheric	<10	Sundin, A., 2008	Cellwood
Microsludge	Chemical /Shear	Ambient	80	<10	Hunt, P. and Wilson, T., 2008	Microsludge
Micropulses	Electric current	Ambient	Atmospheric	<10	Hunt, P. and Wilson, T., 2008	OpenCEL

Although the above technologies are very different in their modes of operation, they all have the same aim, to increase the renewable energy production by increasing the volatile solid (VS) destruction.   VS is a measure of the organic content of the substrate.

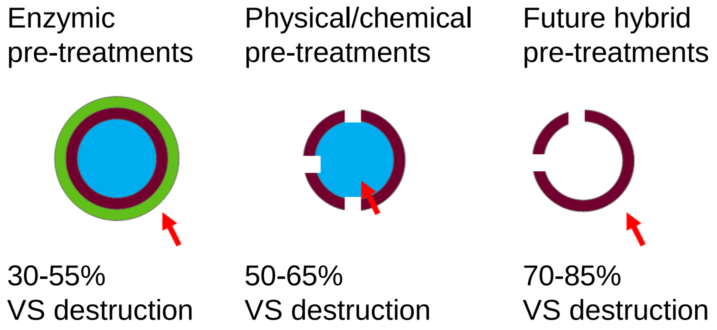

Figure 5 – Modes of operation of substrate pre-treatment technologies and their effectiveness

As illustrated by Figure 5, enzyme-type pre-treatments tend to target the outer coating of the bacteria cell whereas the more aggressive physical and chemical pre-treatments could break down cell wall and target the intra-cellular materials. Currently the best pre-treatment technologies offer a 65% VS destruction rate maximum. In order to achieve greater VFA yield greater VS destruction rates are desirable. Future pre-treatment methods are likely to be hybrids of enzymic and the physiochemical treatments that will be optimised to deliver greater efficiencies with up to 85% VS destruction presently regarded as a realistic target.

4.2 VFA fermentation

VFA from wastes is a new concept; there are still considerable technical challenges to overcome before it can be put into practical applications. Significant progress in VFA production from sewage sludge has already been made and reported (Le *et al*, 2006 and 2007). A major hurdle to its development is believed to be the economic recovery of the compounds. The key to the solution is likely to be the ability to achieve good VFA yields in a high concentration.

Table 6 provides some encouraging early results from the large-scale fermentation trials (80 m^3 batch runs) of VFA production for sewage sludge. The fermented liquor contains high level of VFA (up to 6,370 mg/L as C after 6 days fermentation for an un-thickened sludge).

Table 6 - Summary of the VFA fermentation process trials

Sludge feed	DS %	VS %	pH	total COD	
Average of 7 runs	4.52	72.15	5.72	51,450	
Fermented sludge	SS%	tVFA	pH	total COD	sCOD
Average of 7 runs	2.34	5,580	5.18	41,600	9,392
Fermented liquor	HRT, d	pH	Amm N	COD	tVFA
Batch 4	4	5.2	538	9,360	4,150
Batch 8	6	4.9	450	11,200	6,370
Fermented cake	pH	DS%	*E. coli*	*Salmonella*	
	5.54	27.0	Not Detected	Not Detected	

VS destruction = 67% (Van Kleeck)
TS destruction = 48%
COD destruction = 9850 mg/L (20% of total)

4.3 Alcohol and ester production

The simplest and most effective method for VFA conversion to biofuel is through direct hydrogenation. Hydrogenation of carboxylic acids is well-known and is comprehensively described in the literature. For example, Pesa *et al* (1983) proposed a process for the vapour phase hydrogenation of carboxylic acids to yield their corresponding alcohols in the presence of steam and a catalyst. They claimed that such a process may also be used for the preparation of carboxylic acid esters from carboxylic acids in the absence of steam utilizing the same catalysts. However, providing a low cost, efficient catalyst for the reactions remains a challenge. Reactor design and the optimisation of the reactions also require further development in order to achieve economical fuel production.

5. CONCLUSION

VFA offer a possible and convenient route for biofuel production from waste organic streams. The chemical intermediates may be economically produced on relatively small-scale from different waste sources and locations to allow a distributed production system to be realised. To make VFA suitable for use as a transport fuel, they need to be converted to alcohols or esters, ideally through hydrogenation. The hydrogen source for such a conversion process may be readily provided by the fermentation of up to15% of the VFA. The remaining challenges include more efficient substrate hydrolysis to achieve greater VFA yield; effective VFA recovery and low cost catalysts as well as more innovative reactor designs for economical fuel production.

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