TECHNICAL PAPER

Biorefineries as Sources of Fuels and Chemicals

This paper by GEOFF COVEY[1], BRUCE ALLENDER[1], BRONWYN LAYCOCK[2] and MIKE O'SHEA[3] was presented at the 2013 Appita annual Conference and Exhibition, Melbourne, May 2013.

ABSTRACT

At present, the value of biofuels is such that only large biorefineries are likely to be economic except in special circumstances. Large biorefineries require a large capital investment and thus represent a large commercial risk.

However, there are strategic reasons that make it desirable to some companies to enter the biofuel market now.

Although the revenue from fuels from biorefineries is relatively low, some of the chemicals that form components of these fuels are of high inherent value.

This paper shows that by extracting some chemicals from the products of fast pyrolysis and selling the remainder as fuel, even quite small biorefineries can become economically attractive.

1 Covey Consulting P/L
2 School of Chemical Engineering, University of Queensland
3 CSIRO Materials Science and Engineering

INTRODUCTION

World annual energy demand in 2008* was estimated to be 532 EJ/a and predicted to grow to 812 EJ/a by 2035[1]. Most of the growth is in non-OECD countries, with an average annual growth in demand being 2.3% vs 0.6% for OECD countries.

The largest growth in absolute terms is predicted to be for coal[1]. Renewables have the greatest percentage growth, but this is from a very small base, and their absolute growth is predicted to be slightly less than that of coal. Most of the growth in renewable energy is expected to be in the form of hydro and wind power[1].

Bio-liquids are predicted to rise from 1.8% by volume of total liquid fuel consumption in 2008 to 4.2% in 2035. On an energy basis the quantity of biofuels is much less, and difficult to assess because of the wide range in heats of combustion of different forms of these fuels.

Reserves to production ratios indicate how long currently known reserves of fossil fuels would last at current rates of consumption (Table 1)

Table 1 Changes in Reserves to Production Ratios (in years) for fossil fuels over the last 30 years EIA[1]

	1980	1995	2000	2007	2011
Oil	29	41.4	40.4	42.4	44
Natural gas[2]	56.9	65.7	65	60.1	60.2
Coal		224	209	164	126

The reserves to production ratio of oil continues to rise gradually, and that for natural gas is falling slightly (i.e. the rate of discovery of new reserves is still similar to the rate of consumption) although some of this rise is due to known reserves which were previously regarded as uneconomic becoming economic because of rising prices.

The reserves to production ratio for coal is falling steadily, but this is partly because coal exploration is less vigorous, and known reserves are still very large.

Therefore in the short to medium term, scarcity is not the main driving force for the development of renewable energy; it is the desire to reduce carbon dioxide emissions.

As fossil fuels become more expensive (through scarcity and/or government charges) so renewable energy will become more competitive. Electricity can be generated by a number of means, but matching demand to supply from inherently variable and unpredictable sources such as wind and sunlight will be a major challenge. Steam raising for industrial facilities can be largely from biomass with little or no pre-processing (though the quantities required will be massive).

Despite these possibilities, two problem areas remain – storage of electricity to match times of demand and generation, and liquid fuels for transport.

The big issue will be liquid fuels for transport. Railways can be electrified; there can be a return to some equivalent of trolley busses for urban public transport. Passenger cars and other light vehicles can be battery powered for urban use at least, or can be compressed air powered. However, it is difficult to see how foreseeable technology will enable ships, aircraft and heavy land vehicles to run on anything other than liquid fuels#, and it is here that biofuels must provide the solution.

Eventually fossil fuels must run out but this does not present an immediate incentive to do more than research – carbon taxes in various forms can improve the economics, but still make a very large plant something of a risk (e.g. if change of government leads to a reduction in carbon price).

* The most recent data available. Unfortunately the IEA did not publish an International Outlook in 2012, and the next issue will be published late in 2013.

For ships, nuclear power is of course possible, but so far this has been restricted to military vessels.

ECONOMICS OF SMALL SCALE BIOFUEL PRODUCTION

A change to predominant use of biofuels is unlikely in the near future but there are some special situations in which it can be much more profitable to build medium size biorefineries now. Some examples are as follows:

1. Where the collected and delivered feedstock is very cheap. Traditionally, this has been found to be the case when a biomass waste is generated at a processing plant – in such cases the harvesting and transport costs have already been covered by the primary production, and the biomass is a waste that must be disposed of. Traditional examples included bagasse at sugar mills, empty fruit bunches at palm oil mills, bark, trimmings, saw dust etc. at saw mills and pulp mills and various streams at rubbish tips/ municipal recycling plants. Recent years has seen increasing use of these 'waste' streams as fuel for steam and electricity generation. However, some opportunities still exist, such as where timber is cleared for open-cut mining.
2. In remote areas where the biomass is relatively cheap, but transport costs of conventional fuels to site are high (by analogy, this was the original reason for building the Sasol coal to oil plant).
3. Where some component can be extracted from the bio-product which is of much greater unit value than the fuel, and this can subsidise the cost of fuel production. There are also situations where a high value material can be extracted from the feedstock and the residue, which is the greater part of the feedstock, can then be converted to fuel by a process that would otherwise be uneconomic (e.g. pyrethrum is about 1% of flower heads, the residues can be profitably used as fuel, but the process would be totally uneconomic but for the value of the extract which is the primary product). A possible example in the forest industry would be to collect branches, leaves etc. from the felling site and steam strip high value oils and similar volatiles from them. The residue from this process may then be turned into fuel and other products. In such cases it may be that the main benefit of the extraction process to the economics of the fuel process is that it covers the cost of harvesting and transport of the biomass – i.e. it effectively becomes equivalent to case 1

In simple economic terms there is limited value in making biofuels except at a very large scale.

Considering the case of making fast pyrolysis oil:

- Capital cost is based on the work of Ringer et al.[5] which has been widely used for comparisons of this sort (see e.g. Jones et al.[6]). They estimated a capital cost of USD48.3 million on a 2003 basis for a facility processing 550 od t/d of feedstock. This has been updated to current costs and adjusted for various sizes of plant of 100-1000 od t/d of feed.
- Feed stock price is \$20/od t (residues) or \$100/od t (low grade wood chips or similar).
- Oil yield from fast pyrolysis is assumed to be 75% w/w (at the high end of what is usually assumed). It is assumed that this oil is sold at the same price on an energy basis as bunker oil (USD630/t as at November 2012, Singapore) – again this is very favourable to the bio oil case.
- Carbon tax credit at \$23/t CO_2 for carbon dioxide emissions avoided by substituting a renewable fuel for a fossil fuel.
- For a stand-alone plant, total manning is 22 for plants smaller than 500 t/d feed and 27 for larger plants – average total cost of employment is \$200,000/person.
- It is assumed that the gas and char by-products are used for process fuel and electricity generation. There is usually a small net surplus of electricity (about 588kW for a 550t/d plant[5]). For simplicity, the value of this electricity has been assumed to cover the cost of other utilities.
- Maintenance costs 3% of installed cost/year, insurance 1.5% of installed cost/year.

On this basis the costs of operation and income can be summarised as in Table 2.

This clearly shows that with 'market price' feed stock, biorefineries processing 1000 t/d or less are very uneconomic (at 500 t/d revenues still do not cover operating costs). As feed stock costs are reduced, so the process economics improve, but still several hundred dry tonnes per day of feed are required to be economic (and this is based on very favourable oil yields and selling prices). Also there are very few opportunities to access sufficient feed stock at one site at the low prices required.

Therefore, under present conditions economics favour very large biorefineries.

Production on a scale of several thousand tons/day can become fairly attractive in terms of return on investment, but there are a number of serious risks associated with this:

1. There is no large existing market for bio-fuels unless these are of a direct substitution type, and even then volatility of market price and uncertainty of legislation makes sales on this scale problematic.
2. The capital investment required becomes very large for what is a 'first of kind' project.
3. Securing sufficient feed stock at an attractive price is a problem – existing resources are unlikely to be large enough, and establishing new plantations dedicated to the project usually requires a long lead time (even for short rotation crops) and greatly increases the cost and financial risk.

Table 2 Costs and returns for a small biorefinery making fuel only (costs are in AUD'000)

Plant size od t/d feed	100	200	500	1000
Capital cost	21,000	34,100	64,800	105,300
Annual Operating cost	4967	5322	7150	8243
Oil value	4539	8719	21797	43594
Carbon credit	510	1020	2550	5100
Biomass at $100/od t				
Feedstock cost	3500	7000	17500	35000
Net Annual Cash Flow	-3598	-2583	-303	5450
IRR				**-7%**
Biomass at $20/od t				
Feedstock cost	700	1400	3500	7000
Net Annual Cash Flow	-798	3017	13697	33450
IRR		**1%**	**18%**	**30%**
Biomass at $0/od t				
Feedstock cost	0	0	0	0
Net Annual Cash Flow	-98	4417	17197	40450
IRR		8%	25%	38%

This is for a stand-alone plant. If the biorefinery is integrated with an existing, larger operation (obvious choice being a pulp mill) there can be a significant reduction in administrative overhead. For illustrative purposes it is assumed that manning can be reduced to 13 for small plants and 18 for large ones. It is then also reasonable to assume that the biomass will be at low cost ($20/t).

For companies seeing medium to long term diversification into biorefining as a desirable business strategy there needs to be a more economically attractive means of making an initial entry to the market. This might be done by not restricting manufacturing to fuels, but by also making higher-value chemicals as well. As seen in Table 3, this improves the cash flow, but not sufficiently to make the smaller plants very attractive.

Table 3 Costs and returns for a small biorefinery integrated with a pulp mill making fuel only (costs are in AUD'000)

Plant size od t/d feed	100	200	500	1000
Biomass at $20/od t				
Feedstock cost	700	1400	3500	7000
Net Annual Cash Flow	1002	4817	15497	35250
IRR	**-8%**	**9%**	**22%**	**32%**

CONVENTIONAL CHEMICALS FROM BIOREFINERIES

A number of chemicals for which there is an established market and a high sale price are already extracted from timber or (more often) from leaves or other 'residues. These are commonly extracted by steam distillation or solvent extraction. The spent solids are often discarded, but could form the feedstock for a biofuels plant.

Some examples of high value extractives already marketed commercially:

- Ponderosa pine needle oil USD300/kg in 2006[7]
- Australian Tea Tree oil USD120/kg in 2012[8]
- Sassafras oil USD25/kg in 2012[9]
- Eucalyptus oil USD5-7.50/kg in 2008[10], USD9.80-20/kg in 2012[11]
- Sandalwood oil USD1000-1500/kg in 2012[12 13]
- Cinnamon leaf oil USD 12-20/kg in 2012[11]
- Pine Oil USD 1.2-1.8/kg in 2013 [11]

Note some of these have been fractionated after extraction; the price of the crude extract may be significantly lower.

In general, yields of these oils are low (typically 0.1-1% on od feed). Solvent extraction will usually give a higher yield than steam distillation as it can remove low volatility components, but this extra material may be of different value from the steam extract.

The production methods for these types of chemicals do not result in a liquid biofuel. However, it does provide a solid biomass residue at substantially no cost which can be converted to fuel.

CHEMICALS FROM BIO-FUEL PRODUCTS

Another, and more generally applicable, potential source of high value chemicals is from components of liquid bio-fuels. Useful components can be separated from the product and be sold or converted to more valuable forms. For this paper discussion will be limited to sale of unmodified chemicals and to chemicals/fuels produced by fast pyrolysis of biomass. Similar benefits should be possible for some other processes, but fast pyrolysis has been selected as an example because:

- Fermentation does not produce a wide range of by-products in quantity, and these chemicals are already available from existing fermentation processes.
- Slow pyrolysis (where char production is maximised) gives a lower yield of liquids.
- Limited information is available on the chemical composition of other processes.

Fast pyrolysis involves heating the biomass at about 400-600 °C for a few seconds, usually in a fluidised bed. The feedstock is usually ground to <3 mm and dried before the pyrolysis stage. The process can yield up to 75% liquids.

A typical bio-oil composition given by Bridgwater[14] is shown in Table 4.

Various workers have shown that the proportions of chemicals (and in some cases the actual chemicals produced) can be adjusted by various means including: operating temperature, particle size, feedstock material, catalysis, pre-treatment of the biomass etc.[15 16 17 18 19 20 21 22 23 24 25]. Advantage can be taken of these findings to improve the yields of chemicals of interest and hence the revenue from the biorefinery.

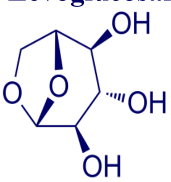
The fuel value of fast pyrolysis oil is about USD180-250/t (depending on the assumptions used). Therefore, any component of the oil which can be sold at a higher price than this has the potential to increase the profitability of the biorefinery PROVIDED that the cost of separating it from the bio-oil does not exceed the price premium.

The economic potential of some of these chemicals will now be considered. It should be noted that the prices quoted are selling prices in multi-tonne lots (in most cases) but the price received by the biorefinery operator will be lower.

Table 4 – Yield of Chemicals from Pyrolysis of Biomass
(Note the figures as presented by Bridgwater add up to well over 100% because of the basis he used. They are adjusted to total 100% in Table 6 below)

Chemical	% by mass
Levoglucosan	30.4
Hydroxyacetaldehyde	15.4
Acetic acid	10.1
Formic acid	9.1
Acetaldehyde	8.5
Furfuryl alcohol	5.2
Catechol	5.0
Methyl glyoxal	4.0
Ethanol	3.6
Cellobiosan	3.2
1,6-anhydroglucofuranose	3.1
Fructose	2.9
Glyoxal	2.8
Formaldehyde	2.4
Phenol	2.1
Propionic acid	2.0
Acetone	2.0
Methylcyclopentene-ol-one	1.9
Methyl formate	1.9
Hydroquinone	1.9
Acetol	1.7
Angelica lactone	1.6
Syringaldehyde	1.5
Methanol	1.4
1-hydroxy-2-butanone	1.3
3-ethyl phenol	1.3

Levoglucosan



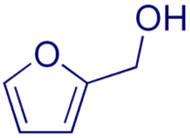
Levoglucosan ((1*R*,2*S*,3*S*,4*R*,5*R*)-6,8-Dioxabicyclo[3.2.1]octane-2,3,4-triol) can be hydrolysed to glucose and other monomeric sugars and hence fermented to ethanol – but this is a very indirect way to convert cellulose to ethanol. It can also be used to synthesise chiral polymers, and its three dimensional structure makes it promising for the production of high rigidity polymers. It can be converted into cross-linkers for fast-curing adhesives and other applications, and has potential applications in the synthesis of pharmaceuticals that require chiral catalysts.

However, at present there is little market for it, and its high price (ca USD50/kg[11]) would not be sustained if demand warranted quantity production.

Hydroxyacetaldehyde

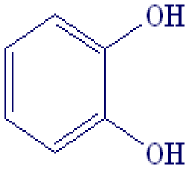
2-Hydroxyacetaldehyde is also known as glycoaldehyde. Although it can take part in many chemical and biological reactions, and is the subject of some patented uses, it does not appear to have any significant commercial use. It is highly soluble in water and very reactive, so steam extraction of this product is problematical. The only price we could find was in quantities of 1-5 g at USD 70-80/g.

Furfuryl alcohol



Furfuryl alcohol (furan-2-ylmethanol) has many applications, and is widely used as a solvent and in the manufacture of resins, adhesives and wetting agents and for timber treatment. It is used in particular for the production of foundry sand binders, as a viscosity reducer for epoxy resins, and as a building block in chemical synthesis, including drug synthesis. Selling price is about USD1600/t[11]

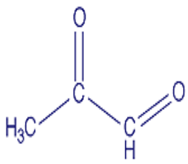
Catechol



Catechol (benzene-1,2-diol) is widely used in the manufacture of pesticides, perfumes and pharmaceuticals, as well as in synthetic tannins, as an anticorrosion agent, an antioxidant in polymers, a bonding agent and as a catalyst. It is produced commercially by the oxidation of phenol with hydrogen peroxide.

Selling price is about USD4000/t[11]

Methylglyoxal

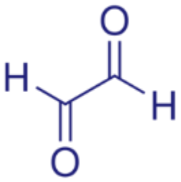


Methylglyoxal (2-oxopropanal) is a reactive chemical that acts against a number of pathogenic microorganisms and is the main active component accounting for anti-microbial activity in manuka honey.

It has potential as a natural anti-microbial and possible anti-cancer agent although it may be cytotoxic[26]. It is used as a pharmaceutical intermediate.

Bulk prices are difficult to determine but Sigma Aldrich[27] offer a 40% solution at AUD 963 for 500 ml. This suggests a bulk price of at least AUD1000/kg on a 100% basis (although recognising that recovery may need to be as an aqueous solution).

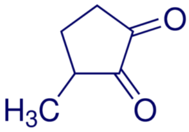
Glyoxal



Glyoxal (ethanedial) is an important intermediate for many chemical applications. It is widely used in the paper and textile industries as a cross-linker, in polymer chemistry, for tanning and for the production of glyoxylic acid and cellulose ethers. It has use as a biocide, sulphide scavenger, and soil hardener. It is also used in the manufacture of imidazoles and other heterocyclic compounds, which are in turn used in pharmaceutical, agricultural chemical and epoxy resin manufacture.

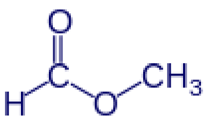
Current world capacity is about 220,000t/a[28]– but production is less than this. Selling price is ~ USD1100/t[11]

Methyl cyclopenteneolone



Methyl cyclopenteneolone (3-methylcyclopentane-1,2-dione) is used as a flavoring and sweet enhancer. It also finds application in other products such as tobacco, detergents and cosmetics.
Current selling price for 25kg lots is ~ USD 40,000/t[26]

Methyl formate



Methyl formate is widely used as a chemical feedstock, particularly in the manufacture of formamides and formic acid, in quick-drying finishes, as a pesticide, to manufacture certain pharmaceuticals and as a low ozone-depletion blowing agent.

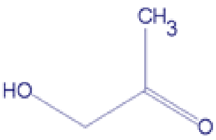
Its selling price is USD1-2,000/t [11]

Hydroquinone

Hydroquinone (benzene-1,4-diol) is used in a range of applications, mainly where it acts as a water-soluble reducing agent. Such applications include antiseptics, skin bleaching agents, photographic developers, and inhibition of polymerisation of chemicals such as methyl methacrylate and acrylic acid. It is also used in some co-polymers.

Its selling price is about USD5000/t.[11]

Acetol



Acetol (1-hydroxypropan-2-one, also known as hydroxyl acetone) is used as a laboratory reagent, a flavouring and as a chemical intermediate.

Selling price USD 20-40,000/t[11]

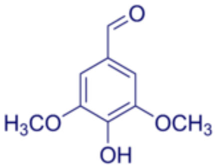
Angelica lactone

Angelica lactone occurs in several different forms, depending on the position of the C=C bond. The structure illustrated here is the β form (5-methylfuran-2(5*H*)-one).

It is used as a flavouring, as a cancer chemo-preventative, and in oral care formulations.

Selling price is >USD 1 million/t (usually sold as 1% solution for USD 10-20/kg [11]).

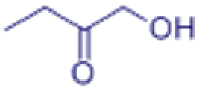
Syringaldehyde



Syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde) is used as a fragrance, a flavouring, as a mediator in hair and fibre dying, and in the production of pharmaceutical intermediates. It has anti-oxidant properties, with potential antifungal and antimicrobial applications (Ibrahim et al. 2012).

Selling price is > USD 1 million/t. (AUD 6340/5kg [26]).

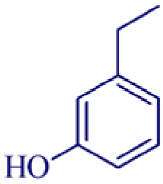
1-Hydroxy-2-butanone



1 - Hydroxy-2-butanone is used as a flavouring and fragrance agent.

Its selling price is USD7000-7500/t [11]

3-Ethylphenol



3-Ethyl phenol is used as a photographic chemical intermediate.

Little pricing information is available (500 mL lots @AUD82.50). Although this suggests a high value product, the market is probably very small and shrinking, so it is probably not worth isolating this compound.

Commodity Chemicals

A number of the chemicals on the list are of a ‘commodity’ type and sell at prices not much greater than fuel oils. However, separation of some of the higher value chemicals may permit the recovery of some of these commodities at little extra cost. Typical selling prices of these chemicals are given in Table 5.

Table 5: Prices for commodity chemicals

Chemical	Selling price USD/t
Acetic acid	4-600[a]
Formic acid	6-700[a]
Furfuryl alcohol	14-1600
Acetaldehyde	900[a]
Formaldehyde	9-1200[a]
Phenol	1400[b]
Acetone	1200[b]
Propionic acid	1600[a]

[a] Alibaba [11]

[b] Platts [29]

Sugars and simple alcohols have not been included in this list as they are unlikely to be worth recovering under any but the most unusual circumstances.

POTENTIAL REVENUE GENERATION

Table 6 shows the potential revenue if all of the chemicals in the fast pyrolysis oil were separated and sold at market price.

In practice the revenue and profit derivable would be much lower:

1. There is a cost in separating components. Some would be relatively easy, others much more difficult. It is usually found that the process required to separate one

product makes recovery of some other products easier because concentrated fractions have been prepared.

2. Not all of the components will be worth recovering – either because of their relatively low value, or because the quantities involved are too small for commercial sales.

Unless the operator markets all the products himself, there will be costs incurred by the distributer/marketer. Despite these constraints, it is reasonable to assume that the profits of the plant could be increased by (say) $500-2,000/t of oil produced.

Also, the markets for some of these products will remain small for the foreseeable future. Therefore, even with new applications for what are currently very expensive chemicals, once a few small biorefineries are supplying the market, there will be little incentive for ‘next generation’, larger biorefineries to compete in the market for these chemicals (just as although the price for vanillin is quite high, very few mills attempt to enter a market which is inherently limited in size).

The cases presented in Table 1 are modified to allow for an extra net contribution of $500 or $2,000/t of feedstock from the production of higher value by-products. As there are many ways in which these by-products might be produced, the contribution is after the additional costs of separating out the by-product have been subtracted from its sale price.

For the current purpose a fixed feed stock price of $100/od t is used for the analyses. In some cases a more expensive feed stock may be required for particular products, but where the feed stock is a residual from harvesting another product (e.g. pine or eucalyptus leaves and twigs) the feed stock cost may be quite low.

The results are given in Table 7.

Table 6 Potential revenue from fast pyrolysis oil components

Component	% w/w	USD/t	Value USD/ t oil
Levoglucosan *	24.1	200	48
Hydroxyacetaldehyde	12.2	1600	195
Acetic acid	8.0	400	32
Formic acid	7.2	600	43
Acetaldehyde	6.7	900	61
Furfuryl alcohol	4.1	1400	58
Catechol	4.0	4000	158
Methyl glyoxal #	3.2	500000	15835
Ethanol	2.9	1100	31
Cellobiosan *	2.5	200	5
1,6-Anhydroglucofuranose*	2.5	200	5
Fructose *	2.3	200	5
Glyoxal	2.2	1100	24
Formaldehyde	1.9	1000	19
Phenol	1.7	1400	23
Propionic acid	1.6	1600	25
Acetone	1.6	1200	19
Methylcyclopenteneolone *	1.5	200	3
Methyl formate	1.5	1200	18
Hydroquinone	1.5	5000	75
Acetol	1.3	20000	269
Angelica lactone	1.3	1000000	12668
Syringaldehyde	1.2	1000000	11876
Methanol*	1.1	200	2
1-hydroxy-2-butanone	1.0	7000	72
3-ethyl phenol *	1.0	200	2
		TOTAL	**41574**

* These components have been assumed to be sold at fuel value.

The price used for methyl glyoxal is conservative

Table 7: Costs and returns for a small biorefinery making fuel and higher value by-products (costs are in AUD'000)

Plant size od t/d feed	**100**	**200**	**500**	**1000**
Capital cost	21000	34100	64800	105300
Annual Operating cost	4967	5322	7150	8243
Oil value	4539	8719	21797	43594
Carbon credit	510	1020	2550	5100
Fuel only with biomass at $100/od t				
Feedstock cost	3500	7000	17500	35000
Net Annual Cash Flow	-3598	-2583	-303	5450
IRR				**-7%**
Fuel only with biomass at $20/od t				
Feedstock cost	700	1400	3500	7000
Net Annual Cash Flow	-798	3017	13697	33450
IRR		**1%**	**18%**	**30%**
Byproducts at $500/t oil, biomass at $100/od t STAND-ALONE				
Feedstock cost	3500	7000	17500	35000
Byproduct revenue	13125	26250	65625	131250
Net Annual Cash Flow	9527	23667	65322	136700
IRR	45%	69%	101%	130%
Byproducts at $2,000/t oil, biomass at $100/od t STAND-ALONE				
Feedstock cost	3500	7000	17500	35000
Byproduct revenue	52500	105000	262500	525000
Net Annual Cash Flow	48902	102417	262197	530450
IRR	233%	300%	405%	504%
Byproducts at $500/t feed, biomass at $100/od t INTEGRATED PLANT				
Feedstock cost	700	1400	3500	7000
Byproduct revenue	13125	26250	65625	131250
Net Annual Cash Flow	11327	25667	67122	138500
IRR	54%	75%	104%	132%
Byproducts at $2,000/t feed, biomass at $100/od t INTEGRATED PLANT				
Feedstock cost	700	1400	3500	7000
Byproduct revenue	52500	105000	262500	525000
Net Annual Cash Flow	50702	104217	263997	532250
IRR	241%	305%	407%	505%

This clearly shows that the addition of the production of a high-value by-product can greatly increase the profitability of making biofuels and can make operation at a scale as small as 100t/d attractive, and if the dual purpose biorefinery is integrated with a pulp mill the profitability is even better.

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