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Fuel Processing Technology xxx (2012) xxx-xxx

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Advanced biofuels from pyrolysis oil...Opportunities for cost reduction **Q3**1

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ARTICLE INFO

 $\mathbf{6}$ Article history: 7 Received 14 November 2011 Received in revised form 5 May 2012 8 9 Accepted 6 September 2012 10 Available online xxxx 12 14Keywords: **B**iofuels 15Pyrolysis oil 1617 Refining Hydrotreating 1819Fast pyrolysis 20Woody biomass 33 32

1. Introduction 34

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Several alternative processes are being developed to produce biofuels 35 from non-edible biomass. They generally fall into one of three categories: 361) biochemical routes to sugars ending with either fermentation to form 37 an alcohol fuel or catalytic conversion to produce conventional fuels, 38 2) gasification followed by biochemical conversion of synthesis gas into 39 motor fuels or alcohols, and 3) fast pyrolysis followed by hydro process-40 ing, which is the topic of this study [1]. Plausible cases have been made 41 that each of these routes can produce transportation fuels from biomass 42at competitive costs in the future. All are still in development and none 43 44 have demonstrated competitive economics versus conventional hydrocarbons on a commercial scale. Early operators of each technology will 45be challenged by the uncertainties and costs associated with pioneer 46 plants. The likely range of costs show substantial overlap given the cur-4748 rent state of each technology. Fast pyrolysis is the least developed of the potential methods to convert woody biomass to transportation fuels 49 and is characterized by more uncertainty but also more potential. A re-5051cent study comparing alternative processes, using corn stover as feedstock [2] showed fast pyrolysis to be the least capital intensive and 52most economical, principally due to the lower complexity of the tech-53 54nology. Its potential to produce conventional motor fuels and to make use of existing refining and logistics infrastructure add to its potential 5556attractiveness.

Biofuel volumes mandated in the Energy Independence and Security 57Act of 2007 (EISA) are the primary driving force for using pyrolysis oil (Pyoil) to make transportation fuel. In a recent study [3] it was estimated

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ABSTRACT

Hydrocarbon derived from fast pyrolysis of plantation wood is a potential feedstock for the production of 21 transportation fuels. Unfortunately, the cost to produce and upgrade this feedstock is highly uncertain, and 22 its current technological state is not competitive with crude oil. Additional R&D will be needed to achieve 23 the significant cost reductions required for competitiveness. Significant technical hurdles must be overcome 24 to achieve a commercially ready, cost competitive technology. This paper identifies the most promising areas 25 for the needed future research. Identification of a stable upgrading catalyst, definition of the maximum level 26 of oxygen that can be tolerated by the existing refining infrastructure, and improved oxygen removal during 27 the pyrolysis step emerge as the most prospective research areas. 28

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that the forest resources and refining concentration located in the South 60 Central United States have the potential to support a mature Pyrolysis 61 Oil industry producing a significant portion of the mandated "Advanced 62 Biofuel" volumes. It is estimated that this region alone could support 63 motor fuels production from Pyoil of 500 kbd or more. Other parts of 64 the U.S. could also support Pyoil value chains, albeit with economics less 65 favorable than the South Central region, and could add to this projected 66 volume. 67

Pyoil's ultimate appeal to the U.S. refining industry will be based upon 68 its becoming an inexpensive feedstock relative to crude oil and/or other 69 renewable fuels. This may be achieved over the course of the time as a re- 70 sult of several factors. 71

Many refiners believe that crude oil will be increasingly supply 72 constrained. This condition could systematically raise crude oil's cost in 73 real terms. The Pyoil feedstock, wood biomass, should not see its costs 74 materially linked to that of crude oil. Some petroleum fuel is consumed 75 in harvesting and logistics, but much of wood biomass production cost 76 involves capital tied up in land/trees and the time value of money be-77 tween planting and harvest. Thus, refiners can look at wood biomass as 78 a feedstock source largely de-linked from crude prices. Wood biomass 79 should therefore become increasingly economic relative to crude over 80 time. The key question is when will this occur. Successful cost reduction 81 R&D will shorten the time when this will occur. 82

2. Methodology

The purpose of this paper is to define research areas that have the 84 largest potential impact for reducing the cost of bio-crude from fast py-85 rolysis of wood. In discussing research opportunities, it is useful to define 86 a base case value chain. For this study the configuration and economics of 87

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the Mature Industry value chain summarized in a recent study [3] will be used (the biomass source is plantation wood shipped via barge to integrated pyrolysis and upgrader plant located on the lower Mississippi River with an overall plant capacity of 20 thousand dry tons/day (kt/d dry) of wood consisting of four 5 kt/d pyrolysis reactors and a single upgrader reactor). Fig. 1 summarizes the value chain and shows the relative contribution of each step.

95This case takes maximum advantage of economies of scale, high concentration of biomass, availability of low cost transportation and 96 97 location in region of high concentration of refining capacity. Note that this case assumes that successful scale up of pyrolysis reactors to 5 kt/d 98 has been achieved (current technology uses 200 t/d reactors) and that 99 a fixed bed reactor is used for the upgrader (a stable upgrader catalyst 100 is found). Failure to scale the pyrolysis reactors to this size and/or having 101 to use a more complex upgrading reactor (cyclic or moving bed) would 102 lead to a higher overall value chain cost but should not materially change 103 the results of this study. 104

In considering various research opportunities, the following adjustments were made. Where changes were made to capital investments the investment related costs are adjusted via (capacity) ^{0.60} for the upgrader and via (capacity) ^{0.7} for the pyrolysis unit except for the pyrolysis reactors. For the pyrolysis reactors, the investment related costs were adjusted via (capacity) ^{0.7} up to a capacity of 5000 tons/day. Above this level, parallel trains for reactors were assumed. In terms of 111 adjustments for upgrader product oxygen levels, 1st order kinetics was 112 assumed and only the upgrader reactor investments were affected. 113 The hydrogen consumption was adjusted using the Veba data [4] for 114 upgrading levels other than the base case. 115

Given that there is a high degree of uncertainty for the capital and 116 total value chain costs, the research opportunity areas were tested 117 with a range of investment cost bases (Pioneer Plant vs. *n*-th plant 118 based contingencies) and are expressed as percentage reduction in 119 total value chain costs. The RAND [5] methodology was used to adjust 120 the upgrader and pyrolysis investment for the pioneer plant cases 121 reflecting the current uncertainties in the technology. As it turns 122 out, while the absolute costs are significantly affected by the contin-123 gency values assumed, the percentage changes by research area are 124 relatively insensitive to these uncertainties and for purposes of this 125 study are virtually identical. Note that all the incentives reported here 126 are not debited for the costs for effecting the potential improvements 127 and therefore represent the maximum incentives available.

3. Results

As reported separately [3], the value chain cost range for the re- 130 fined product entering the existing fuel distribution system would 131



Mature Value Chain

Fig. 1. Mature value chain.

S. Arbogast et al. / Fuel Processing Technology xxx (2012) xxx-xxx

be 3.75 to 5.25 \$/gallon based on today's technology. The estimate 132 133 was made considering only performance that had been demonstrated at the time of this study (200 t/d pyrolysis reactors, recently reported 134 135pyrolysis and upgrader yields) and with favorable assumptions about corrosivity of upgraded pyrolysis oil and successful development of 136an upgrader catalyst system with a one year life. While highly uncer-137tain, these results would suggest that improvements of up to 40% may 138 be needed to bring this technology to be competitive with current 139140 petroleum prices. While some of the economic improvements will come from successful scale up of pyrolysis and upgrader reactors and are es-141 timated to be about 20%, additional improvements of 20% in the base 142technology will be needed to close the gap [3]. 143

Fig. 2 summarizes the results of this study. Given that these are maximum incentives, and do not include the costs required to affect these improvements, one broad observation is that all the potential improvement steps are relatively modest. There does not appear to be a single area of research that emerges that will yield a step change in costs. Rather a combination of improvement steps will be needed.

In looking at the specific R&D areas, upgrader catalyst stability and
 optimization of upgrader/refinery interface emerge as the ones with
 the highest priority. Both areas are characterized by large number of
 uncertainties, but significant potential economic impact.

154The viability of the entire value chain is dependent on finding a 155stable upgrader catalyst. If a catalyst is not identified with life long enough for use in a fixed bed reactor, then the cost and complexity 156of the process increases. This is because more complex reactor sys-157tems must be considered such as cyclic or moving beds. This will in-158159crease the cost of the value chain and increase the complexity and cost of the overall development of the technology. These kinds of re-160 actors would also require that the upgrading catalyst be regenerable. 161

There has been little work done to define the allowable Pyoil oxygen content that the existing refining infrastructure can handle. It appears there are significant cost optimization opportunities at the upgrader/refinery interface. In particular, partial upgrading shows some of the larger incentives identified in this study. This important but complex area will need to be explored at some point before this value chain can be commercialized.

Pyrolysis oxygen removal, plantation and upgrader / pyrolysis yields
 are the next most attractive areas for work. The areas of upgrader catalyst
 selectivity/activity and individual biomass cost reduction steps appear

to have smaller effect on costs. The challenge in all these potential re- 172 search areas is finding low cost improvements that will not significantly 173 erode the incentives shown above. 174

4. Discussion of results

4.1. Hydrotreating improvements 176

The hydrotreater represents one of the higher cost areas in the 177 value chain and improvements here could have a significant cost impact. Catalyst activity, stability and hydrogen selectivity all represent 179 potential improvement areas (upgrader yield is covered separately 180 below), Catalyst stability stands out as a key research area. Currently 181 available catalysts have poor stability, and unless significant progress is 182 made in finding a stable upgrading catalyst, fuel products from Pyoil are unlikely to progress to commercialization. 184

Upgrader catalyst stability is the key uncertainty in the whole Pyoil value chain. The base case value chain discussed in this article assumes a one year upgrader catalyst life and this allows the use of a fixed bed reactor system. There are indications in the literature that current catalyst stability is poor and, moreover, the high hydrothermal conditions in the reactor represent a significant challenge for the integrity of the catalyst support [6]. In fact, there does not appear to be any data in the publicly available literature supporting a Pyoil upgrader catalyst with a multimonth catalyst life. The economics turn out to be particularly sensitive to catalyst life as shown in Fig. 3.

As can be seen, the cost is particularly sensitive to a catalyst with a 195 life less than a year. This is because shorter catalyst life translates not 196 only into higher catalyst costs but also has a significant impact on the 197 service factor of the plant. The base case assumes a service factor of 198 the process to be 90%. If one assumes that it takes two weeks to replace the catalyst, the service factor deteriorates to 86% if the catalyst 200 life is 6 months and to 78% for a 3 month catalyst life. These calculations 201 assume that the other items which contribute to the service factor remain unchanged. Realistically, one would not consider a fixed bed reactor system, if the catalyst life was, in fact, three or 6 months. At this 204 point, other reactor types, such as a cyclic or moving bed, would have 205 to be considered. In these cases, the catalyst would likely need to be regenerable. This change in reactor type would increase the cost and complexity of the process. In addition, the scale up of the process would 208



Fig. 2. Summary of research incentives.

3

S. Arbogast et al. / Fuel Processing Technology xxx (2012) xxx-xxx



Fig. 3. Impact of upgrader catalyst life on costs.

become more costly and time consuming. It should be noted that the incentive for increasing the catalyst life beyond one year diminishes for a catalyst life greater than one year (7% reduction in value chain cost for a catalyst with a two year life). This overall discussion leads to the specific research objective for the upgrader; find a catalyst with at least a one year life.

215 It is found that catalyst activity and hydrogen selectivity have rel-216 atively smaller impacts on costs.

Doubling the activity surprisingly only improves the economics by 217about 2–5%. This is because only the reactor portion of the upgrader 218 investment is impacted. If it assumed that the base case catalyst affects 219 some excess hydrogenation of aromatic structures, then there may be 220an opportunity to develop a more selective catalyst with reduced hy-221 drogen consumption and aromatic saturation. For example, if a 25% re-222223duction in hydrogen consumption (reduce H/C of upgraded Pyoil from 1.75 to 1.33) could be affected, it would be worth about a 2% reduction 224 in costs (the net hydrogen cost which includes some off gas credits 225represents about 8-10% of the total value chain costs in the base case.) 226

227 4.2. Oxygen removal options

Hydrotreating costs are very sensitive to the degree of upgrading required as shown in Fig. 4.

This chart highlights the importance of establishing the minimum 230231level upgrading required because of the high cost of removing the last 232increment of oxygen. In looking for cost reduction opportunities, it is useful to look both upstream and downstream of the upgrader in the 233value chain. Two potential research areas are highlighted on the chart; 234greater oxygen removal in the pyrolysis step and partial upgrading 235236 combined with utilization of the hydrotreating capacity in existing refineries. The key question for each of these areas of research is how 237 these approaches to oxygen removal compare in terms of cost with the 238 base case of severe hydrotreating. 239

240 4.2.1. Partial upgrading / oxygen tolerant refining

The base case in this study assumes that the refinery can handle an upgrader Pyoil containing 0.2% oxygen. Unfortunately, there is very little information on the maximum level of oxygen that can be handled in the refinery processes and products, and what the associated costs are for refining this material. This area has received little attention to date and 245 will have to be addressed at some point if the pyrolysis route to fuels is 246 to be developed. As will be shown below, there could be a large payout 247 in optimizing the upgrader/refinery interface. 248

To define the maximum level of oxygen allowed in existing refineries, 249 one needs to define (1) the corrosion/fouling properties of upgraded 250 Pyoil as a function of oxygen level and boiling point, (2) the impact of ox-251 ygen on the refinery processes, particularly those with sensitive cata-252 lysts, and (3) the impact of Pyoil oxygen on gasoline and diesel product 253 quality. Conceptually, what one is trying to do here is to utilize some of 254 the existing refinery hardware to reduce the Pyoil upgrader severity 255 and investment. Also, the use of the refinery's hydrotreating capabilities 256 which are tailored for specific boiling ranges should potentially improve 257 yields and better utilize hydrogen vs. using the single high pressure 258 upgrader. 259

The sensitivity of the value chain economics to the allowable refinery oxygen level is significant. Given the high cost of removing the last increment of oxygen (Fig. 4), steps which enhance a refinery's ability to tolerate some oxygen in the feedstock could have a significant payout. The key issue is to define the oxygen level where acidity is low enough for safely introducing Pyoil into the refinery. To scope this issue, a brief analytical research was made in the course of this study [3]. Samples of Pyoil^a upgraded to three oxygen levels (8.2%, 4.9% and 0.4% oxygen) were cut into typical refinery fractions and subjected to standard "crude assay" tests.

The results of this initial testing were somewhat surprising. It was 270 observed that for a Pyoil sample upgraded to 4.9% oxygen, the acidity 271 of the heavy fractions (360–1050 °F) was very low as measured by 272 total acid number (TAN).^b The acids appeared to congregate in the 273 light fractions where they are potentially easier to treat. These promising 274 acidity results will need confirmation because they are based on a single 275 set of retained pilot plant samples using only TAN measurements as an 276 indicator of acidity. A more detailed follow-up program on this lead 277 has been developed and is reported elsewhere [3]. This additional testing 278 should pay particular attention to the effects of aging on the pyrolysis oil 279

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^a Samples were provided by **PNNL** from past runs.

^b Total acid number (the amount of potassium hydroxide needed to neutralize acid in the oil) is used by refiners to indicate the corrosion potential of a crude.

S. Arbogast et al. / Fuel Processing Technology xxx (2012) xxx-xxx



Fig. 4. Relative upgrading costs vs. upgrading level.

samples. If these unusual results are confirmed, actual corrosion work on
the heavy fractions would be needed. It should be recognized that while
TAN is useful as an indicator of corrosion for petroleum streams based on
a large amount of experience and data, no such corresponding experience base exists for Pyoil. The primary acids in petroleum are naphthenic, whereas after extensive upgrading of Pyoil the surviving oxygen
species are largely phenolic acids [6].

These results suggest a strategy of partially upgrading Pyoil to only 287 5% oxygen, separating out the 360+ deg F material, which is fed directly 288 289 to a refinery, while further upgrading the light fractions, (light straight run (LSR) and naphtha) to reduce their acidity for safe introduction 290 into the refinery. It was found that the light fractions of the sample 291upgraded to 0.4% oxygen had very low acidity (TAN was below detec-292tion). It is not known what oxygen level (between 4.9% and 0.4%) in 293this fraction needs to be to have a TAN low enough for introduction 294 295 into the refinery. Fig. 5 summarizes this approach. It is estimated that this partial upgrading option would significantly reduce upgrader reac-296 297tor volume (48% of base case) and hydrogen consumption (68% of base 298 case).

It turns out that two factors are very important in determining overall
 attractiveness of this approach; (1) the Pyoil yield from this configura tion and (2) the incremental refining costs for treating this more difficult
 feed.

The economics were tested for a range of partially upgraded (5% 303 304 oxygen) Pyoil yields. If one assumes the yield loss in upgrading to 5% oxygen is all due to oxygen removal (no light ends loss due to hy-305 drocracking), the yield out of the upgrader would be 69% (neglecting 306 any change in the H/C ratio of the upgraded Pyoil). The distillation 307 curves of the three samples in this analytical study mentioned above 308 suggest that significant hydrocracking does not occur until upgrading 309 to between 5% and 0.4% oxygen. The general shape of the hydrogen con-310 sumption curve also supports this assumption. On the other end of the 311 spectrum, if cracking to light ends is assumed to be a function of oxygen 312 removal, then the yield would be closer to 57%. 313

Finding an optimal refining strategy then becomes a significant cost saving opportunity. For this study, the output of the refinery is sumed to be only transportation fuels ex-jet fuel. It was judged that the certification process to make jet from Pyoil based material was too problematic for this study. In terms of the refining of these two streams, the initial thinking is to feed Stream A^c to the naphtha hydrotreater plus 319 reforming/isomerization for octane improvement and feed Stream B to 320 the coker fractionator for conversion/upgrading via hydrocracking and 321 cat cracking. (The diesel fraction was found to be too low in cetane to 322 consider direct blending into product.) An initial cost estimate for this 323 approach indicates the refining costs would increase only by about 324 11% vs. the base case of upgrading to 0.2% oxygen. The key assumptions 325 in estimating the refining costs were that the oxygen was removed as 326 water and the remaining hydrocarbon content behaved as would simi- 327 lar hydrocarbons in conventional refining. It should be emphasized that 328 this estimated cost of refining does not include any unusual costs (cor- 329 rosion protection, process vield and operating cost debits, etc.) to pro- 330 cess these potential bio-crudes. These assumptions would, obviously, 331 have to be confirmed with pilot plant testing. Given that this calculation 332 represents an optimistic refining cost estimate, the economics were also 333 tested with refining costs for handling the partial upgrading Pyoil that 334 are double the base refining costs. 335

Using these various assumptions the incentives for partial upgrading 336 are shown in Table 1. 337

As can be seen the incentive for partial upgrading could be sub- 338 stantial, but is highly uncertain depending on yield and refining cost 339 assumptions. The incentive is highly sensitive to upgrader yield, where- 340 as refining costs have significantly less impact (refining cost are only 341 about 7% of the value chain costs in the base case). These incentives 342 are primarily due to the improved yield of products out of the partial 343 upgrading/refinery combination vs. the base case of upgrading oxygen 344 extinction before refining. The refinery processes appear to be better 345 able to preserve valuable hydrocarbons than does the single high pressure upgrader. 347

^c An alternative option for treating Stream A might be direct product blending vs. octane upgrading via reforming/isomerization. Stream A was found to need some additional octane improvement when upgraded all the way to 0.4% oxygen. It is not known if upgrading to an oxygen level above or below 0.4% will yield a stream with high enough octane for direct product blending. Another significant unknown is how much Pyoil oxygen can be tolerated in the product. Blending off high oxygen content Pyoil into finished product might be more economic than trying to treat it to oxygen extinction. Direct blending into product would have the advantage of avoiding any processing difficulties and costs associated with reforming/isomerizing this stream. This option would obviously require careful product quality testing before consideration.

S. Arbogast et al. / Fuel Processing Technology xxx (2012) xxx-xxx

Base Case Hydroger **Upgraded Pyoil** Upgrader Reactor Raw Pyoil 0.2% Oxyge Partial Upgrading Option LSR + Naphtha Reactor A #2 Hydroger Hydroger 0.4% Oxyggen Raw Pyoll Reactor#1 \$5 Stabilization Reacto Oxyge B Diesel + Jet + Gas Oil + Resid 5% Oxygen Fig. 5. Partial upgrading option.

Even if the analytical results reported above are not duplicated, 348 the discussion above illustrates the kinds of opportunities that are 349 largely unexplored at the upgrader/refinery interface. To progress the 350area of partial upgrading, the key is more fully defining the properties 351 of partially deoxygenated Pyoil as a function of boiling point/upgrading 352 severity, and determining what the maximum level of Pyoil oxygen 353 refineries can safely handle. Some of the first areas to examine, in ad-354 dition to the obvious ones of corrosion and heat exchanger fouling, 355 include (1) defining the feasibility of direct blending of partially 356 upgraded LSR and naphtha streams into gasoline (can some level of 357 upgrading produce material with high enough octane to avoid catalytic 358 processing?), (2) establishing how much of the partially upgraded Pyoil 359 360 oxygen species can be tolerated in gasoline and diesel (can blending into product be used instead of extra upgrading to get rid of oxygen?) 361 and (3) defining the need to hydrotreat partially upgraded Pyoil prior 362 to cat cracking (where can hydrotreating in the refinery be avoided?). 363 Broadly, what one is looking for are strategies that use blending as 364

an alternative to catalytic processing and that minimize processing that requires use of expensive hydrogen. Depending on what is found as the limiting factor, potential additional areas to study include oxygen tolerant refinery catalysts, improved corrosion management of Pyoil specific acids and fuel additives to offset any product quality issues found. These overall research areas are largely unexplored.

371 4.2.2. Oxygen removal at pyrolysis step

The overall motivation for removing some of the oxygen in the pyrolysis step is premised on the idea that this can be done more cost effectively than accomplishing all removal at the upgrader. More specifically, pyrolysis stage oxygen removal could realize a twofold cost

t1.1 Table 1

t1.2 Incentives for partial upgrading.

t1.3	Assumed upgrader yield	Assumed refining	Cost incentive
t1.4	Optimistic (69%)	Optimistic (+11%)	17%
1.5	Pessimistic (57%)	Optimistic (+11%)	9%
1.6	Optimistic (69%)	Pessimistic (2× Base)	11%
1.7	Pessimistic (57%)	Pessimistic (2× Base)	3%

saving; (1) reducing the net upgrading costs by removing oxygen as 376 carbon oxides vs. using expensive hydrogen and reducing the upgrader 377 size/investment and (2) producing a Pyoil product that is more stable, 378 making it easier to move logistically and for the upgrader to handle. 379

The base process produces a raw Pyoil containing 30-40% oxygen. 380 It is known that extensive modification of pyrolysis, as represented by 381 the liquefaction process,^d does, in fact, produce a product with signif- 382 icantly lower oxygen content (12-14%) [7] and is more stable and 383 easier to handle in the upgrading step [6]. Unfortunately, the cost of 384 the liquefaction process largely offsets the benefits of a less costly 385 upgrading step [8]. If modifications could be found that are significantly 386 less costly than liquefaction, they would be of interest. Shell's HTU pro- 387 cess attempts to simplify and reduce the cost of this process by eliminat- 388 ing the catalyst and carbon monoxide [9]. A more recent effort is Gas 389 Technology Institute's IH [2] process [10] (combined hydropyrolysis 390 and hydroconversion process), where its hydropyrolysis product is 391 reported to be ~2% oxygen. RTI International, in collaboration with 392 ADM, ConocoPhillips and Albemarle, recently received an ARPA-E con- 393 tract to develop a "single-step catalytic biomass pyrolysis process with 394 high carbon conversion efficiency to produce stable bio-crude with low 395 oxygen content (<10%)" [11]. KiOR, a Houston based company, is pursu- 396 ing another approach [12]. They are looking at a catalytic fluid bed process 397 to convert the biomass and remove oxygen. Product oxygen from this 398 process has not been reported. They are currently constructing a 500 t/d 399 plant in Columbus, MS. 400

Possibilities that could be explored in this area might include changes 401 in the operating conditions in the pyrolysis unit including the use of catalysts, hydrogen donors or hydrogen as well as various feed pretreatment 403 and product post treatment steps to reduce the oxygen content of the raw Pyoil without sacrificing hydrocarbon yield. One could even consider genetically modified trees tailored to the pyrolysis step. A lack of understanding of the impact of feedstock properties on Pyoil oxygen significantly limits opportunities in this area however. 408

In setting a research target for pyrolysis oxygen removal, a Pyoil level 409 of 10 wt.% oxygen (dry basis) was chosen based on the performance of 410

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 $^{^{\}rm d}$ In the liquefaction process wood is slurried with water, recycle oil product and a sodium carbonate catalyst at high temperature (350 °C) and pressure (20.8 Mpa) with carbon monoxide.

S. Arbogast et al. / Fuel Processing Technology xxx (2012) xxx-xxx

the liquefaction process which could be considered a surrogate for a 411 modified pyrolysis process. Higher target levels of oxygen could be con-412 413 sidered, but are believed to have separation and handling problems be-414 cause of (1) similar density of Pyoil and water, (2) increased viscosity of the Pyoil and (3) the potential for significant dissolved hydrocarbon loss 415 in the waste water [6]. If one selects this as a target for modifying the 416 pyrolysis process, the potential reduction in the value chain costs is esti-417 mated to be 7-9%. The actual savings achieved would be offset by any 418 419 incremental cost in the pyrolysis step required to accomplish this target. Again the challenge is to affect oxygen removal in the pyrolysis step at 420 421 low cost. The additional (and possibly more important) benefit of oxygen removal at the pyrolysis step is that the reported severe catalyst 422 423 fouling/deactivation in the upgrading step might be significantly re-424 duced. There is clear evidence that the product from the liquefaction process mentioned above displays reduced upgrader catalyst fouling 425and deactivation [13]. 426

427 4.3. Yield improvement incentives

The yield from both the pyrolysis and upgrading steps has a signif-428 icant effect on the economics. For the *n*-th plant analysis done by PNNL 429 430 [13], the yields used assumed significant progress in yield from now 431 until the *n*-th plant was built; such assumptions are typical and not unreasonable for this kind of study (in their study they assumed the 432 pyrolysis yield was 0.65 lbs raw, dry Pyoil / lbs dry wood and 0.55 433 lbs upgraded Pyoil/lbs. of raw dry Pyoil.). In terms of the pyrolysis 434 435step, current literature values vary widely [14], especially if residues (bark, foliage) are included. The value used for the *n*-th plant is at 436 the very upper end of literature values and is for heartwood. Residues 437and bark/thinnings give lower yields (51% and 53% vs. 60% from heart-438 439wood) which seem to correlate with lower volatiles and higher ash content. Some researchers have shown acid treating of wood to re-440 441move ash from wood does, in fact, improve pyrolysis yields [15]. Recent studies directly comparing pyrolysis of heartwood vs. whole 442 trees have shown yields for whole trees to be 6% to 9% lower than 443 for heartwood [16]. A more realistic estimate of current technology 444445 pyrolysis yield, therefore, would be about 58%. The reported yields above are from very small laboratory studies. It is not known how 446 well these small scale yields survive the scale up to commercial sized 447 pyrolysis reactors, given the sensitivity of bio-oil yields to vapor phase 448 residence time and temperature. This further argues for using a lower 449 yield to represent current technology vs. the PNNL basis above. 450

In terms of upgrading yields there is limited recent information
available. Early data from VEBA [4] reported yields of ~45 wt.%
(upgraded Pyoil/raw, dry Pyoil). More recent information [17] measured yields in the 48–54% range. Again the data are from small scale
laboratory units. For this paper the base case upgrader yield selected
was 50%.

Table 2 quantifies the impact of increasing pyrolysis and upgradingyields on value chain costs.

459Note that these calculations assume that the product oxygen from 460 each process step remains the same as the yields are improved. Yields from both the upgrader and pyrolysis units are important as the over-461 all yield improvements are the arithmetic product of the yields from 462 463 each step. The value chain cost reduction for yield improvements in 464 both steps is about 13%. In the pyrolysis step, potential yield improvement areas might include exploring feed pretreatment to remove ash 465or to add a catalyst. In the upgrader, finding a catalyst that shows 466

t2.1 Table 2

t2.2 Impact of pyrolysis and upgrader yields on value chain costs.

t2.3	Process step	Base yield	Potential future yield	Value chain cost reduction
t2.4	Pyrolysis	58%	65%	6%
t2.5	Upgrading	50%	55%	6–7%

lower cracking to light ends might represent an opportunity area. The 467 key issue is the cost of achieving these improvements. 468

4.4. Biomass research

The costs of producing, harvesting, chipping and shipping the bio- 470 mass component account for up to 48% of the total fuel cost plus return 471 in our models, depending mostly on location, and provide a substantial 472 opportunity for research and development leading to cost reduction. In- 473 creasing the dry biomass yield per acre/year has the greatest impact on 474 the total quantity of fuel products that can be sustainably produced 475 using the technology. Higher yields allow more concentrated production 476 and collection, which would reduce shipping costs. To the extent that 477 yields are high enough to support large scale pyrolysis operations locat- 478 ed close to the biomass resource, savings as high as 9% of total value 479 chain costs could be obtained without losing the economies of scale of 480 centralized pyrolysis. Reduction in plantation and harvesting/chipping 481 costs by 25%, influenced in part by more concentrated biomass produc-482 tion, could reduce the value chain cost by 5% and 4%, respectively. 483

Longer term potential lies in modifying biomass composition to better 484 suit the pyrolysis and upgrading processes. Materials that would require 485 less preparation produce Pyoil with less oxygen, lower water content, 486 and/or lower trace element content would provide cost and operational 487 benefits. Specific programs and objectives in this area were beyond the 488 scope of our study, 489

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A competitive pyrolysis value chain will require a combination of 491 significant technical advances from the current state of the technology. 492 The two largest technical uncertainties affecting the value chain's viability 493 are (1) upgrader catalyst life and (2) the allowable level of Pyoil oxygen 494 the existing refinery infrastructure can handle. Once these are defined, 495 optimization of oxygen removal in the value chain both upstream and 496 downstream of the upgrader, and plantation/upgrader/pyrolysis yields 497 appear to have the greatest impact on the overall economics. These represent the research areas with the highest potential for cost reduction. 499 The ultimate challenge is to make progress in these areas while not eroding the projected savings. 501

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Please cite this article as: S. Arbogast, et al., Advanced biofuels from pyrolysis oil...Opportunities for cost reduction, Fuel Process. Technol. (2012), http://dx.doi.org/10.1016/j.fuproc.2012.09.022

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S. Arbogast et al. / Fuel Processing Technology xxx (2012) xxx-xxx

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