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Comparison of Fuel Yield of Biomaterials Between Fast Pyrolysis and Gasification

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Abstract: Pyrolysis is a viable method of extracting combustible fuels as gases or liquids from various, high carbon and hydrogen containing biomaterials. This Meta-study attempts to find the ideal combinations of processes for maximising biofuel output by comparing a range of biomaterials (cotton stalks, algae and peach scraps), put through the two primary methods of pyrolysis, through analysis of reactor type, Temperature, particle size and lower heating value achieved from biofuel output. It is proposed that the fast pyrolysis of Algae in a Fluidized bed reactor at a temperature of 550°C is the optimum combination of parameters for maximising biofuel output in terms of bio-oil yield and lower heating value (LHV) in kJ/kg.

Keywords: Pyrolysis; Gasification; lower heating value; Biochar; Bio-oil; Syngas



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Table 1: Nomenclature

<i>Pyrolysis</i>	Is using the application of heat (Temperatures often at 430°C or higher) to chemically decompose organic/carbon-based material. Being distinct as the process takes place in the absence or near absence of oxygen [1-2].
<i>Gasification</i>	Is a high temperature process intended to yield primarily gaseous products from input reactants. These reactions usually occur at around 600-900°C with short residence times. Gasification reactions ideally take place in a reactor specifically designed for this process and those similar to it, such as a plug flow reactor, or a fixed bed reactor [3].
LHV	The lower heating value (also known as net calorific value) of a fuel is defined as the amount of heat released by combusting a specified quantity (initially at 25°C) and returning the temperature of the combustion products to 150°C, which assumes the latent heat of vaporization of water in the reaction products is not recovered [4].
Biochar	Charcoal produced from plant matter and stored in the soil as a means of removing carbon dioxide from the atmosphere.
Bio oil	Pyrolysis oil, sometimes also known as bio crude or bio oil, is a synthetic fuel under investigation as substitute for petroleum. It is extracted by biomass to liquid technology of destructive distillation from dried biomass in a reactor at temperature of about 500 °C with subsequent cooling.
Syngas	A mixture of carbon monoxide and hydrogen produced industrially, especially from coal, and used as a feedstock in making synthetic chemicals.

1. Introduction

Pyrolysis is a viable method of converting bio-waste or otherwise unusable organic matter into solid, liquid and gaseous, high carbon, biofuels [1, 5, 6]. There is an obvious need for cleaner, more cost effective energy sources in the world and while environmental benefits and socio-economics are not the focus of this Meta study they are still worth mentioning. While biofuels would have a similar impact upon the environment as the products are similar to those of petrol and diesel, the process of obtaining biofuel from organic matter is one that favours the environment whilst having a potential fraction of the cost of mining and using fossil fuels. In 2007 the average global food waste was ~1.6 Gigatonnes [7]; not including the non-edible plant matter that goes unused in other agricultural practices such as cotton farming, some of this can be used for pyrolytic conversion. Even though biofuels are not equipped to be the solution to global warming, despite their significant advantage in the reduction of greenhouse gases, there are still cleaner energies. However in developing countries, obtaining biofuels from pyrolysis is a very viable method for energy production and therefore research into this area should continue [8,9].

The process of converting biomaterial into solid phase, high carbon content biochar and a mixture of non-condensable gases and organic vapours is pyrolysis. Organic vapours can be condensed into bio-oils and acid extract [1, 2, 6]. Through pyrolysis, the chemical decomposition of carbon-carbon bonds occur that then form carbon-oxygen bonds, to form a range of different molecules such as

aldehydes, carboxylic acids, phenols, etc. These can then be further combined into esters and large polymers with a final liquid result of bio-oils and acids. The products are broken into states of matter, solids being carbon rich bio-char that does not vaporise at high temperatures, the liquids are long carbon chain bio-oils and aqueous phase acids such as acetic acid, and gases that are low-weight simple molecules primarily carbon monoxide, water and methane, with trace amounts of nitrogen depending on the feedstock used [10].

The processes of fast pyrolysis and gasification have been chosen as the focuses of this meta study. Through the comparison of these two processes with variables including the materials used, analysis of reactor type, catalyst and final enthalpy achieved from biofuel output, the meta study may determine the most efficient combination of these variables to give the optimal parameters for bio-oil and syngas production as a combination of yield and LHV.

2. Methods

In this meta study, research databases were consulted using the search terms “Pyrolysis”, and “Biomass” to find research publications. The search was then restricted to the years 2014-2017. This timeframe was chosen as it gave the most recent information in this field. Finally, the papers were limited strictly to those with greater than 5 citations and greatest relevance to the finding the most efficient parameters for maximum biofuel and LHV. With this background information, parameters were defined to two processes (gasification and fast pyrolysis) and investigation began looking specifically for commonly used materials.

After finding the common materials used in both processes (cotton stalks, peach scraps and algae) with the data available, a comparison was made. Through analysis of the experimental reports, the common results found were the bio-oil yield and the temperature of the reactor was operated. More research was done with no restrictions on the year of publication or the citation tally. However, reports had to include bio-oil yield and temperature for a comparison and analysis of the results.

We found the heat energy input using literature values for heat capacity for the materials of interest and determined their LHV. With these new results, we constructed graphs in order to make it easier to analyse the materials and processes, also allowing for trends to be seen.

Further data was collected to determine how reactor type and particle size affected the processes, including captive sample reactor, fixed-bed reactor, plug flow reactor and fluidized-bed reactor and the effect that both had on a combination of yield and LHV of fuel. Again the search had no restriction on the year of publication or citation tally.

With all of the variables analysed and accounted for, a final comparison was made in order to give the optimal parameters for maximising bio-energy output. The LHV was multiplied by the percentage yield in order to compare the overall variables.

However, research continued to investigate how reactor type and particle size affected the processes. This was done by researching using the same material and process parameters but focusing on variables in the prior sentence. When the references had been collected, comparison was made between the captive sample reactor, fixed-bed reactor, plug flow reactor and fluidized-bed reactor. As well as the comparison on the effect of particle size, and what the effect both had on the heat energy input.

With all of the variables been Analysed and accounted for, a final comparison is made in order to give the optimal parameters for maximising bio-energy output. The LHV is times by the percentage yield in order to compare the overall variables.

Throughout the duration of making this report, it was peer reviewed by other students, academics and Dr Schulte. They gave feedback allowing us to continually improve our report. This was done weekly in order to maximise our time and effort.

3. Results and Discussion

3.1.1: Cotton stalks

Fuel conversion of cotton stalks is a well-researched area [11-14]. The pyrolysis test researched was carried out inside a captive sample reactor over a temperature range of 400-760C, using an average cotton stalk particle size of 1mm diameter. LHV values for bio-oil was 17770 kJ/kg [15] and for syngas 13840 kJ/kg which was not the highest achievable but this will be discussed further. Carbon content determined through elemental analysis was found to be 44.29%, hydrogen was 5.57% and oxygen was 49.4% [15]. The study concluded that maximum bio-oil yield (45% v/v) at 550C and a syngas yield (84% v/v) at 760 C [12].

For gasification the reaction was carried out in a fixed bed gasifier over a temperature range of 750-950C, using the same 1mm particle size. LHV value for syngas was 11090 kJ/kg which was not the highest achievable but this will be discussed later. Elemental analysis remains the same as the material is the same. The study concluded that the maximum syngas yield (56% v/v) occurs at 950C [11].

In both methods it was mentioned that the LHV for syngas was not at its highest. Syngas is a mixture of mainly Carbon Dioxide and Hydrogen meaning the amount of energy released when combusted relies heavily on the ratio between these gases.

For pyrolysis a yield of 84% at 760C gave a LHV of 13840 kJ/kg and had a H₂/CO ratio of 0.86. However the highest LHV of syngas (14800 kJ/kg) was measured at 460C however with a lower yield of 63% v/v and a H₂/CO ratio of 0.46.

For gasification a yield of 56% v/v at 950 gave a LHV of 11090 kJ/kg and had a H₂/CO ratio of 0.93. However the highest LHV (11620 kJ/kg) was measured at 900C however with a lower yield of 49.25% v/v and a H₂/CO ratio of 0.84 [11].

The heat capacity of cotton stalks used, are in the range of 1.3-1.5 kJ/kg/k [16]. For the fast pyrolysis of cotton stalks at 550 C, assuming heating from 25 C it was calculated the minimum input energy to be ~ 735 kJ/kg. For gasification at 950 C, assuming heating from 25 C, it was calculated the minimum energy input to be ~ 1295 kJ/kg.

3.1.2: Algae

Fuel conversion of algae via pyrolysis was carried out in a fluidised bed reactor over a relatively low temperature of 485 C, using an unspecified particle size, however the algae was flocculated meaning the particle size likely did not exceed 1mm. LHV for bio-oil was 33770 kJ/kg. A result of LHV for syngas produced from algal pyrolysis wasn't given likely due to the lack of production since pyrolysis favours liquid fuel and high temperatures favour gases. Carbon content, determined through elemental analysis was found to be 54.32%, Hydrogen was 6.85% and oxygen was 34.35%. The study concluded that the yield for bio-oil at 485 C was 17.4% m/m [10, 17].

For gasification the reaction was carried out in a plug flow reactor over a very low temperature of 350C and a pressure of 20684 kpa, once again using an unspecified particles size but are likely no larger than 1 mm. We calculated LHV value for syngas was 29566.50 kJ/kg. Carbon content determined through elemental analysis was found to be 43.4% Hydrogen was 5% and Oxygen was 30.7%. The study concluded that at a temperature of 350 C the yield of syngas was 69% v/v [18].

The heat capacity of algae was found to range between 3.625-4.125 kJ/kg/K [19]. It calculated that at the temperature of the fast pyrolysis reaction of 485 C, assuming heating from 25 C, the minimum input energy for the reaction would be ~ 1785 kJ/kg. We calculated that for the gasification reaction at 350 C, the minimum input energy would be around ~ 1260 kJ/kg.

3.1.3: Peach scraps

Fuel conversion of peach scraps via pyrolysis was carried out in a fixed bed reactor over a temperature of 550C using a particle size of 1.25mm. LHV for bio-oil was 27830 kJ/kg. Carbon content, determined through elemental analysis was found to be 45.6%, hydrogen was 6.9% and oxygen was 46.5%. The study concluded that the yield for bio-oil at 550C was 22.4% v/v [20].

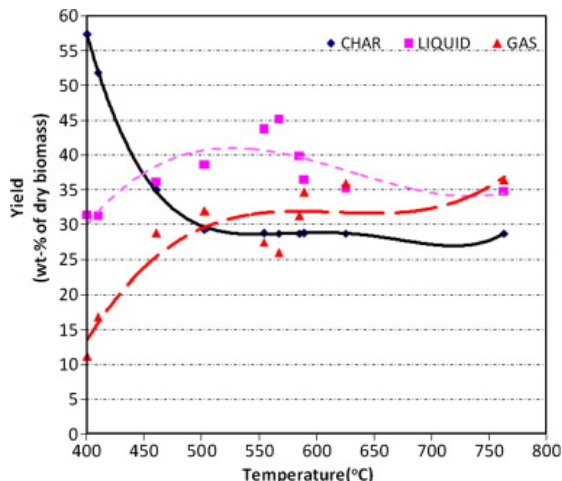
For gasification the reaction was carried out in a plug flow reactor over a temperature of 550C and pressure of 25000 kpa. LHV for syngas was 15238 kJ/kg converted from a value of HHV by dividing by 1.05 [21]. Carbon content, determined through elemental analysis was found to be 41.2%, hydrogen was 6.7% and oxygen was 51.4%. The study concluded at a temperature of 550 the yield of syngas was 44% [22].

The heat capacity of peach products was found to range between 3.64-3.81 kJ/kg/k [23]. Applying this to the fast pyrolysis reaction and gasification reaction at 550C, we calculate that, assuming heating from 25 C, a minimum energy input of ~1955 kJ/kg is required.

3.2 Effect of Temperature

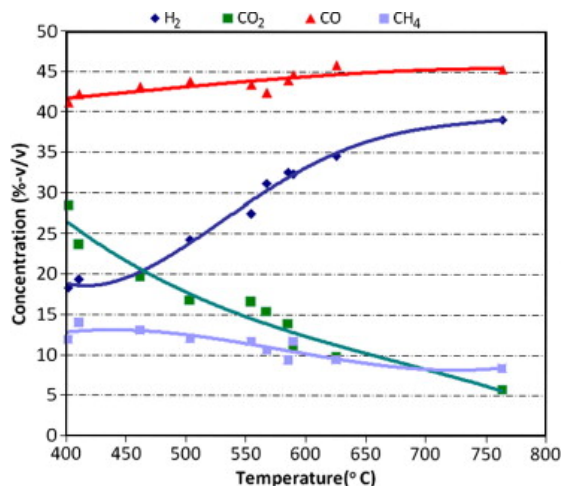
From results obtained and fig.1, it is shown regardless of the process, the higher the temperature of the reaction vessel the higher the yield of gaseous products. At ~300C both liquid and gaseous fuel yields begin to significantly increase. The graph shows that at ~500-550C the maximum liquid yield are reached and gaseous yield plateaus. After this temperature, the liquids decompose and thermally crack into smaller gaseous molecules such CO₂ and H₂, and as a result, gaseous and biochar yield increases. Hence gasification at high temperatures or high pressures, produce a higher yield of syngas. Whereas mid-range temperatures are better to an extent, for liquid bio-oil yield [11].

In terms of composition of gaseous yield, high temperatures favour higher CO and H₂, production as seen in Fig 2. Considering syngas is the ideal product consisting of hydrogen and carbon monoxide and dioxide, higher temperatures are ideal. Both methane and carbon dioxide decrease as temperature increases and since they are not an ideal component of syngas, this is beneficial to the quality, and thus the LHV of the syngas. Therefore in order to maximise quality of syngas, higher temperatures are beneficial. This is to the extent of a hydrogen concentration plateau, where in energy put into the system to heat up biomass would be rendered too high to justify the output. This high yield for high temperature trend was observed across all materials researched and they were recorded in section 3.1. Note that the highest syngas yield for any process was the pyrolysis of cotton stalks and is due to the type of reactor used which is discussed in section 3.3.



Fuel yield by weight versus Temperature

Figure 1. Displays the percentage yield of each state of matter product (solid, liquid, gaseous) occurring over a temperature range of 400-760°C. Points of trend intersection are where two states produce the same yield at a given temperature [11].



Concentration of constituent gases versus Temperature

Figure 2. Displays the percentage concentration of the primary gases extracted via pyrolysis as temperature increases. The trend line intersections show that for a given temperature two gases may be produced in the same quantity [11].

3.3 Effect of Reactor type

For legitimate comparison of results obtained, it is necessary to study the difference between the different reactor types used. There are 4 main reactors used in the observed experiments: captive

sample reactor, fixed-bed reactor, plug flow reactor and fluidized-bed reactor. The most important factor when examining these reactors is heat transfer rate [24].

Captive sample reactors are small laboratory scale reactors that are intended for experimental use. These reactors are not in any way suitable for industrial use, though they provide much higher heat transfer rates than other reactors and minute control of variables for experimental purposes [25].

Fixed bed reactors are a commonly used reactor in the chemical engineering industry, with both the reactants and catalyst in a dry state. These reactors typically have slow heat transfer rates, resulting in low liquid yields. This means that they are sub-optimal for usage in fast pyrolysis reactions, where a high yield of liquid products is ideal [26].

Plug flow reactors are long tubes, where the various phases move along the length of the reactor. These reactors generally have high heat transfer rates which makes them ideal for both fast pyrolysis and gasification. A plug flow reactor is best used when most phases are in a gaseous state, therefore gasification reactions are more favourable than fast pyrolysis [27].

Fluidized bed reactors are similar to fixed bed reactors both in design and usage, they are a commonly used reactor type for chemical engineering. The reaction occurs in a liquid state, with a gas catalyst being pumped into the reactor. The high heat transfer rate makes this process ideal for fast pyrolysis reactions where high liquid yields are important [26].

The ideal reactor for a pyrolysis reaction therefore depends on the reaction type. Fixed bed reactors are sub-optimal due to low heat transfer rates and higher solid yields [26, 28]. Captive sample reactors, while having significantly higher heat transfer rates than any other reactors, are not useful to consider due to a complete lack of industrial viability [25]. For a fast pyrolysis reaction, a fluidized bed reactor is ideal due to its high heat transfer rate and high liquid yields [24, 26]. For gasification reactions, a plug flow reactor is ideal due to high heat transfer rate, and the fact that plug flow reactors favour mostly gaseous phases [24, 27, 28].

3.4 Effect of Biomass Particle size

We found that diameter of particle size has an impact on the yield of gaseous products in particular and is described in Fig.1. and in other papers [14, 29].

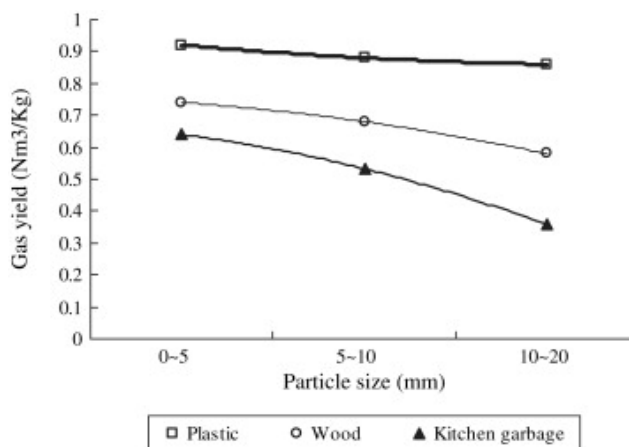


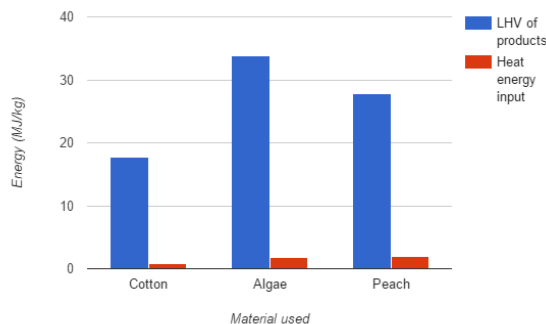
Figure 3. Displays the relationship between the yield of syngas and the size of the particles that undergo pyrolysis. For this meta study the relevant material is wood. [30]

This study focuses on biomass as feedstock so wood is the focus in fig 3. In chemical composition, wood is similar to other biomaterials, so it is safe to assume trends observed in this graph are consistent with would be observed for cotton stalks, algae and peach scraps. It is seen that a smaller particle size between 1-5 mm yields higher gas content [14, 29]. Due to the larger surface area, heating works more thoroughly over a shorter residence time, producing less char residue. However, in materials composed of longer carbon chain molecules, larger particle size favours longer residence time, resulting in long carbon chains being broken down into lighter chemical constituents i.e. gaseous fuels [11].

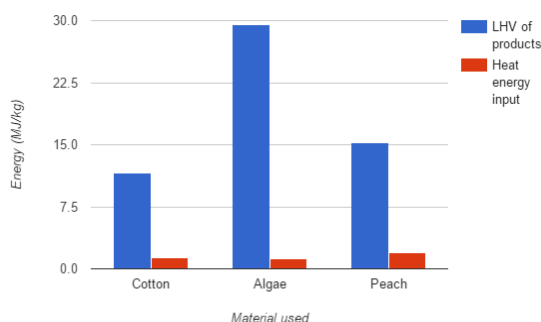
3.5 Meta-study Analysis

Results from this meta study show that for fast pyrolysis, Algae products have the highest total LHV at 33.77 MJ/kg [10,17] with a heat input of 1.785 MJ/kg. Peach products have an LHV of 27.83 MJ/kg [20] with a heat input of 1.955 MJ/kg, and Cotton products have an LHV of 17.77 MJ/kg [27] with a heat input of 0.735 MJ/kg. These findings are summarised in Fig. 4.

The final results for gasification show that Algae products have the highest total LHV at 29.566 MJ/kg [18] with a heat input of 1.26 MJ/kg. Peach products have an LHV of 15.238 MJ/kg [22] with a heat input of 1.955 MJ/kg, and Cotton products have an LHV of 11.62 MJ/kg with a heat input of 1.295 MJ/kg [11]. These findings are summarised in Fig. 5.



Heat input and LHV output for fast pyrolysis of cotton stalks, algae, and peach scraps.
Figure 4. Compares the heat input for each material in a fast pyrolysis reaction with the LHV of the products

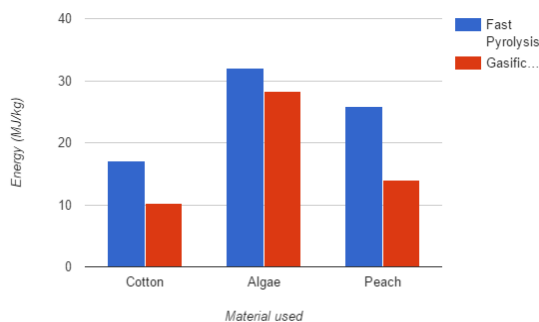


Heat input and LHV output for gasification of cotton stalks, algae, and peach scraps
Figure 5. Compares the heat input for each material in a gasification reaction with the LHV of the products

For final comparison of fast pyrolysis and gasification of Cotton stalks, Algae, and Peach scraps, heat energy input values were subtracted from their respective product LHV values to determine net energy production. Net energy production is how much energy in terms of heat input is required to run the reaction in comparison to how much energy can be gained from combustion of the products.

The net energy production from fast pyrolysis reactions were highest for Algae with a total of 31.985 MJ/kg, Peach scraps was found to be 25.875 MJ/kg, and Cotton stalks was found to be 17.035 MJ/kg.

The net energy production from gasification reactions were also highest for Algae with a total of 28.306 MJ/kg, Peach scraps was found to be 14.045 MJ/kg, and Cotton stalks was found to be 10.325 MJ/kg. These findings are summarised in Fig. 6.



Net energy production (Output-Input) for fast pyrolysis and gasification of cotton stalks, algae, and peach scraps.

Figure 6. Compares the net energy production from fast pyrolysis reactions and gasification reactions across three different materials.

The fast pyrolysis of algae was performed in a fluidized bed reactor, this reactor is optimal for fast pyrolysis on an industrial scale (as detailed in 3.3). The gasification of Algae was carried out in a plug flow reactor, this reactor is optimal for gasification on an industrial scale (as detailed in 3.3). Therefore, both reactions should be expected to yield similar LHV values in products on the industrial scale to their respective reactions in this meta study.

The fast pyrolysis of cotton stalks was carried out in a captive sample reactor, this reactor yields products with higher LHV than would be expected in industrial scale reactions (as detailed in 3.3). The gasification of Cotton Stalks was performed in a fixed-bed reactor, these reactors are sub-optimal for all pyrolysis reactions (as detailed in 3.3). Therefore, gasification reactions in optimal industrial environments should be expected to produce higher LHV products than shown, and similarly, fast pyrolysis reactions should be expected to produce lower LHV products than shown.

The fast pyrolysis of Peach Scraps was performed in a fixed bed reactor, this reactor yields products with lower LHV values than should be expected in industrial scale reactions (as detailed in 3.3). The gasification of Peach scraps was performed in a plug flow reactor, these reactors are optimal for gasification reactions on an industrial scale (as detailed in 3.3). Therefore, fast pyrolysis reactions on an industrial scale should be expected to produce higher LHV products than shown, and gasification reactions should produce similar LHV value products to what is shown.

4. Conclusions

This meta-study suggests that the ideal combination of variables is that of the fast pyrolysis of algae in a fluidized bed reactor at a temperature of $\sim 550^{\circ}\text{C}$, is the optimal parameters for maximizing biofuel output and LHV. The LHV for the bio oil produced algae was found to be 33770kJ/kg [10], which was found to be significantly higher than that of 17770kJ/kg [11] for cotton stalks and the 27830kJ/kg [20]

for peach scraps. For all materials compared, the LHV values for fast pyrolysis were all greater than that of gasification, illustrating that fast pyrolysis is superior in efficiency when producing biofuels. The temperature between $\sim 550^{\circ}\text{C}$ [11] is optimal for producing bio oils, whereas syngas is optimized at a higher temperature $\sim 760^{\circ}\text{C}$ [11]. The analysis of the differing reactor types demonstrated that both methods of biofuel production favored high heat transfer rates. While the plug flow reactors were found to be the most effective during gasification due to the phases being mainly in a gaseous phase[26], where as in the fluidized bed reactor the reactions occur in a liquid state so fast pyrolysis is the most efficient[27].

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